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Articles

Poly(2,5-diphenylgermole): Incorporation of a Germole Ring into a Conjugated Polymer

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The intramolecular zirconocene coupling of 4,4-bis(hexyloxymethyl)-1,7-bis-*p*-halophenyl-1,6-heptadiynes provides 2,5-bis-*p*-halophenylzirconocyclopentadienes (bromo and chloro derivatives), which undergo efficient transmetalation reactions with $GeBr_4$. Methylation of the resulting dihalogermoles with MeLi provided bis-*p*-halophenyl-2,5-germole monomers. These functionalized germoles were polymerized via nickel coupling to give oligo- and poly(2,5-diphenylgermole) materials (**7**). Investigations of optical properties reveal that the monomers and a model 2,5-bisphenylgermole are somewhat photoluminescent ($\Phi = 0.018-0.12$), while the high molecular weight polymer ($M_n \approx 20\,000$) exhibits very efficient photoemission ($\Phi = 0.79$). Electrochemical studies indicate that delocalization in **7** is accompanied by a modest lowering of the LUMO level relative to that of the monomer.

Introduction

Significant efforts have been expended toward the preparation and characterization of soluble π-conjugated polymers with various structures, in attempts to access interesting and useful optoelectronic properties.[1] The incorporation of siloles and germoles into conjugated polymers is of special interest, given computational studies that suggest that silole rings have small band gaps and a low-lying LUMO.[2] Thus, polymers incorporating these units might be expected to exhibit novel charge-transporting properties for use in polymer-based electronic devices. However, the preparation of macromolecules containing silole monomer units has proven difficult due to limited routes to the 2,5-difunctional siloles needed for polymerization. There have been several recent reports of the incorporation of siloles into conjugated polymers,[3] such as silole−thiophene,[3a,c] silole−acetylene,[3f] and silole−pyrole[3d] alternating polymers. Recently, Tamao's group has succeeded in preparing the first poly(2,5-silole).[3i] These silole-containing polymers and oligomers exhibit significantly lower energy optical absorption maxima than related phenylene-, thiophene-, and pyrole-containing polymers and oligomers. However, conjugated systems containing germole groups have received far less attention, and no germole-containing polymers have been reported to date.[3j,4]

We have been investigating use of the zirconocene coupling of diynes[5] for the preparation of a variety of polymers and macrocycles.[6] Using this method, we have obtained a range of new conjugated polymers via reactions of zirconocyclopentadiene units in the polymer backbone. In addition, we have prepared conjugated polymers from the regioselective zirconocene coupling of poly(arylenediyne)s.[6h,i] The resulting zirconium-containing polymers were hydrolyzed to the corresponding poly(arylenediene)s, for which electronic properties are readily varied via appropriate choice of the arylene group. Using this modular exchange of components in

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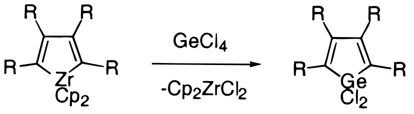
the polymer backbone, we have obtained polymers with tunable optical absorption and emission maxima.[6h]

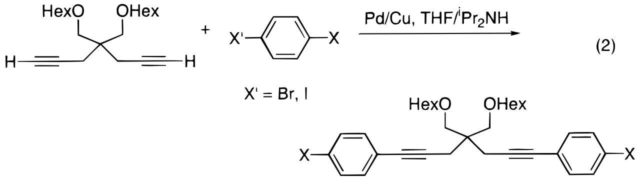
We report here the synthesis of poly(2,5-diphenylgermole) and an investigation of its optoelectronic properties. Our synthetic approach takes advantage of the metallacycle transfer from zirconium to germanium, initially reported by Fagan and Nugent (eq 1).[7] A modification of this reaction has allowed synthesis of 2,5-bis-*p*-halophenylgermoles, which can be polymerized via nickel-mediated couplings.[8]



(1)

Results and Discussion

Monomer Synthesis. Diynes **1a** and **1b** were obtained in high yield by the palladium-catalyzed cross-couplings of 4,4-bis(hexyloxymethyl)-1,6-heptadiyne with 1-bromo-4-chlorobenzene and 1-bromo-4-iodobenzene, respectively.[9]

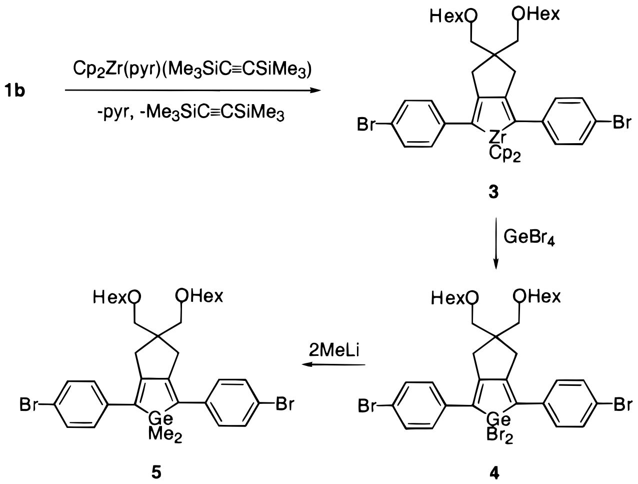


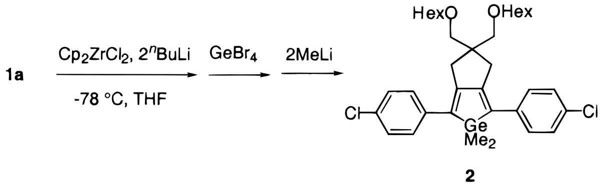
(2)

1a, X = Cl; **1b**, X = Br

The 2,5-bis-*p*-halophenylgermole monomers **2** and **5** were synthesized via the three-step procedures outlined in eq 3 and Scheme 1. For **2**, a one-pot reaction was employed. The intramolecular zirconocene coupling of **1a** in THF proceeded with no apparent complications resulting from the presence of chlorophenyl functionalities, to afford a deep red solution of the zirconocyclopentadiene. This solution was treated with $GeBr_4$, to produce the germole dibromide as a synthetic intermediate, and then MeLi to give **2** in 61% yield as a bright yellow oil after purification by column chromatography. Alternative procedures employing the transmetalation reagents $GeCl_4$ and Me_2GeBr_2 gave lower overall yields. The chemical structure of **2** was confirmed by NMR and IR spectroscopy and by high-resolution mass spectrometry. Freshly prepared monomer **2** was found to give better results in the polymerization reactions described below.

Scheme 1





(3)

The synthesis of **5** is outlined in Scheme 1. The intramolecular coupling of **1b** employed the zirconocene reagent $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$[10,11] and was carried out in benzene at room temperature to give a red solution from which the zirconocyclopentadiene **3** was isolated as a red oil in 83% yield. This coupling procedure is tolerant of the bromophenyl functional groups in **1b**, and no appreciable side products could be detected in the crude product (by NMR spectroscopy). Treatment of **3** in THF at −78 °C with $GeBr_4$ afforded the dibromogermole compound **4**, which was subsequently converted to **5** by treatment with MeLi at −78 °C in Et_2O. Pure monomer **5** was obtained by washing the crude, vacuum-dried reaction mixture with cold pentane and then extraction of the product into benzene to remove it from LiBr. The benzene was removed under reduced pressure to afford **5** as a bright yellow oil.

Polymer Model Compound Synthesis. The polymer model compound **6** was synthesized by a procedure similar to that used for monomers **2** and **5**. Intramolecular zirconocene coupling of 1,7-diphenyl-1,6-heptadiyne followed by transmetalation with $GeBr_4$ and alkylation with MeLi yielded **6** (31%) as a bright yellow powder after purification by column chromatography (eq 4).

The molecular structure of **6**, as determined by X-ray crystallography (Figure 1), is similar to that of other crystalline germole derivatives.[4a,12] The germole ring is almost planar, and no unusual distortions of the diene

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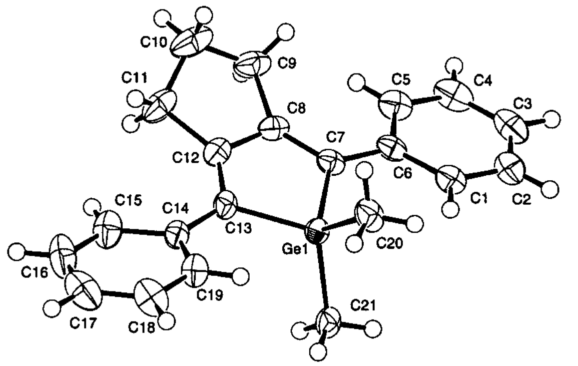
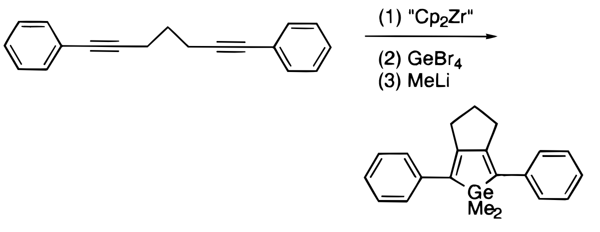


Figure 1. X-ray crystallographic structure of model compound 6.



(4)

6

moiety or phenyl groups are evident. The dihedral angles between the least-squares plane of the germole ring and the two phenyl rings are 12° and 24°. This suggests that conjugation along the backbone of phenylene−germole polymers is not optimal, as expected.

Polymer Synthesis. A diphenylgermole polymer was first prepared via the zerovalent nickel-mediated homocoupling of **2** (Scheme 2). This synthesis is based on the method of Colon and co-workers for the preparation of biaryls and polyaryls utilizing a mixture of NiCl$_2$, Zn, triphenylphosphine, and bipyridine in dimethylacetamide (DMAc).[8c,d] We observed that higher molecular weights were obtained with activated zinc, rigorously anhydrous conditions, and high monomer purity. The reaction mixture was heated to 70 °C for 20 min, resulting in a deep red solution, indicating the formation of the active nickel coupling reagent, to which was added a DMAc solution of **2**. The resulting mixture was allowed to stir for 3 days at 70 °C and was then poured into methanol. Filtration and removal of solvent from the supernatant gave a small amount of oligomers (**7a**; $M_n = 1900$; PDI = 1.2) as a yellow oil. The remaining precipitate was dissolved in THF and reprecipitated with methanol to give polymer sample **7b** as a yellow solid (25% yield). The molecular weight of polymer **7b**, determined by gel permeation chromatography (GPC; polystyrene standards; $M_n = 4700$; PDI = 1.9), is similar to that determined by end group analysis ($M_n = 3800$; DP ≈ 7, by ^{1}H NMR integration). Attempts to increase the molecular weight of **7b** via this synthetic procedure were unsuccessful, so an alternative method was developed.

Recent reports on improved aryl−aryl coupling methods prompted us to employ a reagent consisting of Ni(COD)$_2$ and bipyridine in DMF/toluene solution.[13] Addition of monomer **5** to this reagent at 60 °C resulted in a red solution, from which the polymer was isolated as a bright yellow solid (**7c**, 88%) after precipitation with methanol (Scheme 2). This material is visually similar to **7b** but has a much higher molecular weight (M_n = 20 000, PDI = 2.9) and correspondingly different optical properties.

Optical Properties. The photophysical properties of **2**, **5**, **6**, and **7a**−**c** were investigated in dilute deoxygenated chloroform solution. Absorption and emission data are summarized in Table 1, and Figure 2 presents absorption and emission spectra for **7b**, which are representative for the series of polymer samples described here. All samples of polymer **7** exhibit λ_{max} values in their absorption spectra that are significantly red-shifted with respect to values for poly(*p*-phenylene),[14] indicating a greater degree of delocalization in **7**. The optical absorption for **7** is also red-shifted with respect to that for poly(diphenyl-1,4-*cis*-dienylene) (λ_{max} = 396).[6i] This is presumably due to either a decrease in steric interactions along the polymer chain allowing better orbital overlap and a longer conjugation length or a lowering of the LUMO level in the π-system by incorporation of the germole ring. Emission spectra of all compounds investigated are independent of the excitation wavelength (over a range of 350−450 nm), and the excitation spectra reproduce the corresponding absorption spectra. There is a substantial shift in the absorption maxima of **7** relative to that of **6** (40 nm for **7a**, 66 nm for **7b**, and 78 nm for **7c**), suggesting that the conjugation length of the polymer extends well beyond seven repeat units. In addition, the photoluminescence quantum yields were found to be dependent on the polymer molecular weight, with higher molecular weight corresponding to a greater quantum yield.

For **7a**−**c**, the wide range in absorption λ_{max} values precludes the use of a single standard for the quantum yield determination. A solution of quinine in sulfuric acid (λ_{max} = 350 nm) was used as a fluorescence standard in most cases, as its absorption overlaps significantly with those of **2**, **5**, **6**, and **7a**. For **7b** and **7c**, [Ru(bipy)$_3$][PF$_6$]$_2$ in MeCN (λ_{max} = 450 nm) was also used. When irradiated at 440 nm, the observed quantum yields for **7b** and **7c** were much higher and in proportion to the lower values obtained with the quinine standard (Table 1). Clearly, in these cases, use of the [Ru(bipy)$_3$][PF$_6$]$_2$ standard is most appropriate.

Electrochemistry. Further insight into the electronic structure of **7** was obtained by comparing its electrochemical behavior with that of model compound **6**. The cyclic voltammogram of **6** in THF solution exhibits an irreversible reduction at −3.02 V vs Fc/Fc$^+$, while polymer **7c** undergoes quasi-reversible reduction at −2.66 V. This shift in redox behavior between model compound (monomer) and polymer parallels trends observed for silole-containing polymers[2a,3] and polythiophene[15] and is consistent with the expected drop in the HOMO−LUMO gap accompanying increased con-

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Scheme 2

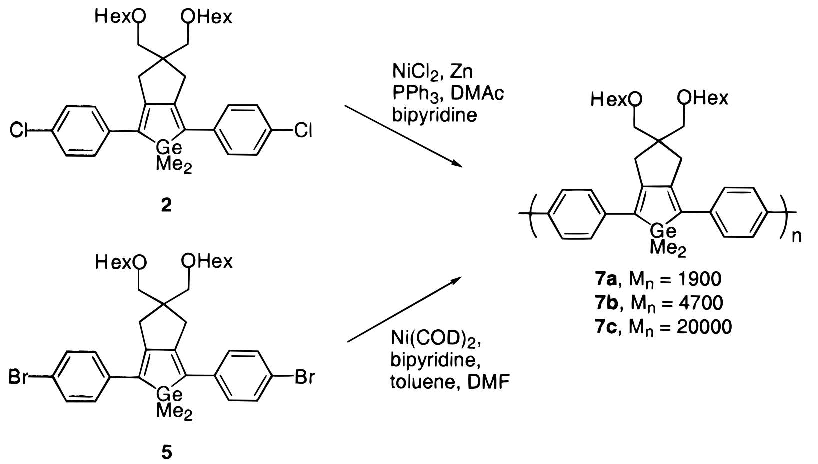

Table 1. Optical Properties of Germole-Containing Materials

compound	λ_{max} (nm) absorption	λ_{max} (nm) emission	Φ^{350}	Φ^{440}
2	368	457	0.084	
5	376	464	0.12	
6	364	452	0.018	
7a, $M_n = 1900$	404	486	0.059	
7b, $M_n = 4700$	430	498	0.14	0.52
7c, $M_n = 20000$	442	500	0.21	0.79

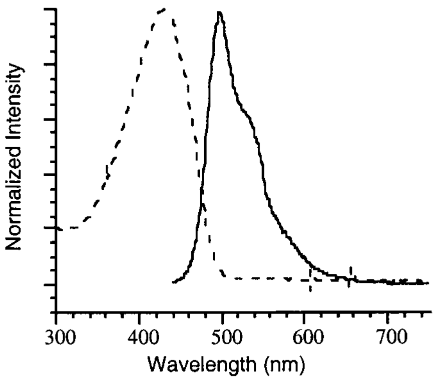

Figure 2. Absorption (- - -) and emission (—) spectra of **7b** (M_n = 4700).

jugation. However, the polymer and model compound oxidize at similar potentials. The oxidation waves for both **7c** and **6** are weak in THF and appear only as broad, ill-defined features, both centered at approximately 0.6 V. For an acetonitrile solution of **6**, an irreversible reduction wave was observed at −2.53 V, and distinct oxidation waves appeared at 0.75 and 1.21 V. Unfortunately, polymer **7c** was insufficiently soluble in acetonitrile for analysis, but measurements on film samples revealed a broad oxidation feature centered around 0.8 V. No reduction behavior could be observed for films of **7c** within the potential limits of the instrument. The observation that oxidation potentials are similar while the reduction potential decreases moderately from monomer to polymer suggests that a decrease in the energy of the LUMO is the primary mechanism by which the band gap in the polymer is decreased with increasing conjugation. This is in keeping with recent theoretical and experimental investigations by Tamao on silole-containing oligomers and polymers.[3]

Concluding Remarks

In this contribution we have described the first route to germole-containing polymers, via zirconocene-coupling chemistry. As we have recently reported elsewhere,[16] the zirconocene-coupling reaction is tolerant of chloro- and bromophenyl groups, allowing the synthesis of 2,5-bis-*p*-halophenylzirconocyclopentadienes, which are readily converted to functionalized monomers. In the chemistry described here, functionalized germoles were polymerized with incorporation of germole rings into the polymer's main chain. The optical properties of this polymer indicate considerable delocalization and a conjugation length that is greater than about 7 monomer units (or 21 rings). For comparison, we have recently determined (based on studies with discrete oligomers) that the conjugation length in phenylene-thiophene-1-oxide and phenylene-thiophene-1,1-dioxide chains is 15−20 rings.[17] Interestingly, **7** displays photoemission properties that are strongly dependent on chain length over the molecular weights investigated. The sample with highest molecular weight (ca. 20 000) is strongly emissive, suggesting possible applications in light-emitting devices. Electrochemical studies indicate that delocalization in **7** is accompanied by a modest lowering of the LUMO level relative to that of the monomer. Future investigations will further probe the electronic properties of this and related structures, obtained via zirconocene-coupling routes to well-defined oligomeric species.

Experimental Section

General Comments. Organometallic reagents were stored and handled under nitrogen atmosphere in a glovebox or using Schlenk techniques. Toluene, THF, benzene, pentane, and diethyl ether were dried by distillation from K/benzophenone under N$_2$. DMAc, DMF, and acetonitrile were dried by distillation from CaH$_2$ under N$_2$. Pd-catalyzed coupling was carried out using ^{i}Pr$_2$NH that had been sparged with nitrogen for 30 min before use. All NMR spectra were obtained using Bruker AMX-300, AMX-400, or DRX-500 spectrometers. Infrared spectra were recorded on a Mattson Infinity FTIR spectrometer, and UV−visible spectra were recorded on an HP 8452A instrument. Elemental analyses and mass spectra were ob-

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tained at the University of California, Berkeley Microanalytical Facility and Mass Spectrometry Facility. Electrochemical measurements were carried out using a BAS 50W potentiostat using a standard cell consisting of a Pt disk working electrode, a Pt wire counter electrode, and a reference electrode containing silver wire and 0.01 M $AgNO_3$ in dry acetonitrile. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile or dry THF. Ferrocene was used as an internal standard ($E_{1/2}$ for $Fc/Fc^+ = 0$) for measurements involving a soluble species and as an external standard for film measurements. Compound **6** was analyzed as a 0.1 M solution in THF or acetonitrile, and polymer **7c** was analyzed as a saturated solution (ca. 6 mg/g of THF with 0.1 M electrolyte). Films of **7c** were cast onto the working electrode by allowing a concentrated THF solution to evaporate in a glovebox. The film-coated electrodes were then exposed to vacuum for ca. 10 min. Reduction and oxidation scans were run on separate samples of films, due to the irreversible nature of the redox processes observed. All scans were initiated at or near zero, and the potential was ramped at rates ranging from 200 to 500 mV/s. All measurements were carried out with the cell in a Vacuum Atmospheres glovebox with an argon atmosphere. Photoluminescence measurements were performed using a Spex FluoroMax fluorimeter on optically dilute ($A \approx 0.06$ in 1 cm quartz cell), degassed solutions of the sample. Quantum efficiencies were calculated as described[18] using either quinine in degassed 1 N H_2SO_4 or $[Ru(bipy)_3][PF_6]_2$ in dry, degassed acetonitrile as emission standards. $Cp_2Zr(pyr)(Me_3SiCCSiMe_3)$ was synthesized according to the literature procedure.[10a]

4,4-Bis(hexyloxymethyl)-1,6-heptadiyne. This compound was prepared from 4,4-bis(hydroxymethyl)-1,6-heptadiyne via a modified literature procedure.[19] A 1 L Erlenmeyer flask was charged with 4,4-bis(hydroxymethyl)-1,6-heptadiyne (24 g, 158 mmol), 1-bromohexane (59 g, 360 mmol), potassium hydroxide (36 g, 640 mmol), and DMSO (500 mL). The reaction mixture was allowed to stir for 10 h at room temperature. The reaction mixture was then poured into 1 L of H_2O and extracted with Et_2O (3 × 250 mL). The solvent was removed by rotoevaporation, and the residue was purified by column chromatography (10% EtOAc in hexanes). This yielded 4,4-bis(hexyloxymethyl)-1,6-heptadiyne (83%, 42 g) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, $J = 5.1$, 6 H, CH_3), 1.28 (m, 12 H, CH_2), 1.53 (quint, 4 H, CH_2), 1.95 (t, $J = 2.1$, 2 H, CCH), 2.35 (d, $J = 2.1$, 4 H, CCH_2), 3.38 (s, 4 H, OCH_2), 3.41 (t, $J = 4.8$, 4 H, OCH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0 (CH_3), 21.8, 22.6, 25.8, 29.5, 31.7 (CH_2), 71.7 (CC_4), 70.12, 71.2 (OCH_2), 71.4 (CC), 80.9 (CC). IR (neat, KBr, cm^{-1}): 3311, 2956, 2931, 2860, 2798, 2119 (CC), 1466, 1429, 1375, 1117, 636.

4,4-Bis(hexyloxymethyl)-1,7-bis-*p*-chlorophenyl-1,6-heptadiyne (1a). A 500 mL Schlenk flask was charged with 1-bromo-4-chlorobenzene (5.9 g, 31 mmol), $Pd(PPh_3)_4$ (0.20 g, 0.17 mmol), CuI (0.10 g, 0.52 mmol), $^iPr_2NH$ (50 mL), and THF (100 mL). To this solution under N_2 was added 4,4-bis(hexyloxymethyl)-1,6-heptadiyne (4.8 g, 15 mmol). The solution was allowed to stir at room temperature for 3 days. During this period a substantial amount of white precipitate formed. Pentane (100 mL) was added to the reaction mixture, which was then washed with dilute NH_4OH (75 mL, 1.0 M) and H_2O (75 mL). The organic layer was dried with Na_2SO_4, and the solvent was removed by rotoevaporation. This yielded **1a** (67%, 5.5 g) as a clear oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, $J = 6.6$, 6 H, CH_3), 1.30 (m, 12 H, CH_2), 1.56 (m, 4 H, CH_2), 2.61 (s, 4 H, CH_2), 3.45 (t, $J = 6.5$, 4 H, CH_2), 3.47 (s, 4 H, OCH_2), 7.28 (d, $J = 8.2$, 4 H, C_6H_4), 7.32 (d, $J = 8.5$, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7, 23.3, 25.9, 29.6, 31.7, 42.8 (CH_2), 71.7, 71.9 (OCH_2), 81.5, 88.1 (CC), 122.5, 128.5, 132.5, 133.5 (C_6H_4). IR (neat, KBr, cm^{-1}): 2930, 2860, 2224, 1897, 1652, 1489, 1466, 1428, 1375, 1288, 1094, 1015, 827, 524. Anal. Calcd for $C_{33}H_{42}O_2Cl_2$: C, 73.17; H, 7.83. Found: C, 72.87; H, 8.00.

4,4-Bis(hexyloxymethyl)-1,7-bis-*p*-bromophenyl-1,6-heptadiyne (1b).[16] 1-Bromo-4-iodobenzene (11 g, 40 mmol), 4,4-bis(hexyloxymethyl)-1,6-heptadiyne 4 g, 20 mmol), $Pd(PPh_3)_4$ (0.42 g, 0.36 mmol), and CuI (0.14 g, 0.73 mmol) were dissolved in 100 mL of THF under nitrogen. After addition of 40 mL of diisopropyamine, the resulting solution was stirred for 2 days. The white precipitate was removed by filtration. The filtrate was diluted with hexane and washed with 10% NH_4OH, water, and brine. After drying over $MgSO_4$, the solvents were removed under vacuo. The oily residue was subjected to column chromatography on silica gel, eluting first with hexanes followed by mixture solvents (hexane/ethyl acetate = 10:1), to obtain **1b** as a colorless oil (10 g, 83%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, $J = 10.5$, 4H), 7.25 (d, $J = 11.0$, 4H), 3.46 (s, 4H), 3.43 (t, $J = 6.5$, 4H), 2.60 (s, 4H), 1.55 (m, 4H), 1.53−1.26 (m, 16H), 0.87 (t, $J = 7.5$, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 133.0, 131.4, 123.1, 122.2, 88.3, 81.9, 71.8, 71.6, 42.8, 31.6, 29.5, 25.8, 23.2, 22.6, 14.0. Anal. Calcd for $C_{33}H_{42}Br_2O_2$: C, 62.86; H, 6.71. Found: C, 62.53; H, 6.75.

$C_{35}H_{48}GeO_2Cl_2$ (2). A 250 mL Schlenk flask was charged with Cp_2ZrCl_2 (3.0 g, 11.0 mmol) and 150 mL of dry THF. This solution was cooled to − 78 °C in a dry ice acetone bath, and ^nBuLi (8.6 mL, 2.45 M, 21.0 mmol) was added dropwise over 5 min. The resulting solution was allowed to stir for 15 min at −78 °C, and then **1a** (4.5 g, 10.0 mmol of diyne) in 10 mL of dry THF was slowly added over 5 min. The reaction mixture was allowed to stir under N_2 while the cold bath slowly warmed to room temperature over 3−4 h. Stirring was continued for an additional 1 h at room temperature. The zirconocyclopentadiene was not isolated but was converted directly to the intermediate dibromogermole by addition of $GeBr_4$ (1.6 mL, 13 mmol) at 0 °C. The reaction mixture was allowed to stir for 24 h at room temperature, and then the solvent was removed under vacuum. The resulting residue was washed with pentane (3 × 75 mL) to separate the intermediate dibromogermole from the zirconocene dibromide. The pentane was removed, and the intermediate dibromogermole was redissolved in 150 mL of THF. The reaction mixture was cooled to −78 °C, and MeLi (12.6 mL, 1.43 M mmol, 18.0 mmol) was added dropwise over 5 min. The solution was allowed to slowly warm to room temperature over 3 h and was then stirred for an additional 1 h at room temperature. Diethyl ether (100 mL) was added to the reaction mixture. The resulting mixture was washed with dilute HCl (150 mL, 0.5 M), H_2O (150 mL), dilute $NaHCO_3$ (150 mL, 1.0 M), and H_2O (150 mL). The organic layer was dried with Na_2SO_4, and the solvent was removed by rotoevaporation. The crude product was purified by column chromatography (25% toluene in hexane). This yielded **2** (61%, 4.3 g) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.65 (s, 6 H, $GeCH_3$), 0.90 (t, $J = 6.5$, 6 H, CH_3), 1.26 (m, 12 H, CH_2), 1.52 (m, 4 H, CH_2), 2.65 (s, 4 H, CH_2), 3.32 (s, 4 H, OCH_2), 3.39 (t, $J = 6.6$, 4 H, OCH_2), 7.27 (m, 8 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −0.8 ($GeCH_3$), 14.0 (CH_3), 22.6, 25.8, 29.5, 31.7, 36.3, 50.0 (CC_4), 71.5, 73.6 (OCH_2), 128.6, 129.1, 131.4, 134.6, 138.4, 155.2 (C_6H_4 and C_4Ge). IR (KBr, cm^{-1}) 2955, 2930, 2858, 1661, 1588, 1487, 1465, 1243, 1109, 1013, 827. Anal. Calcd for $C_{35}H_{48}GeO_2Cl_2$: C, 65.24; H, 7.52. Found: C, 64.33; H, 7.64. HRMS (EI): Calcd for $C_{35}H_{48}GeO_2Cl_2$: 644.2226. Found: 644.2226.

$C_{43}H_{52}Br_2O_2Zr$ (3). A 150 mL Schlenk tube was charged with $Cp_2Zr(py)(Me_3SiC_2SiMe_3)$ (1.18 g, 3.0 mmol) and 25 mL of benzene to give a very dark red solution. To this was slowly added a solution of **1b** (1.63 g, 3.0 mmol) in 10 mL of benzene until the deep red color changed to light red-orange. The solution was stirred at room temperature for 2 h and was then

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[18] (a) *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1, Chapter 8, p 231. (b) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

[19] Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

frozen and exposed to vacuum. After sublimation of the benzene a red oil remained. This oil was dissolved in benzene, and the resulting solution was frozen and exposed to vacuum to sublime away the benzene and remove other volatiles. This procedure was repeated to remove bis(trimethylsilyl)acetylene. The resulting red oil contained only small amounts of the alkyne and was pure enough for use in subsequent reactions. This product can be further purified by crystallization from pentane. Cooling of a very concentrated solution of crude **3** gave fluffy orange-red microcrystals after 2 days at −40 °C. Two recrystallizations gave analytically pure **3** (2.12 g, 2.50 mmol, 83%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.86 (t, J = 5.4, 6 H, CH_3), 1.18−1.26 (m, 12 H, CH_2), 1.45−1.53 (m, 2 H, CH_2), 2.60 (s, 4 H, CH_2), 3.29 (s, 4 H, OCH_2), 3.33 (t, J = 5.0, 4 H, OCH_2), 5.75 (s, 10 H, ZrCp), 6.82 (d, J = 6.3, 4 H, C_6H_4), 7.43 (d, J = 6.3, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 14.3 (CH_3), 20.3, 26.3, 30.0, 32.0, 40.5, 49.7 (CH_2), 71.8, 73.7 (OCH_2), 110.4 (ZrCp), 114.1, 117.8 (GeC_4), 125.8, 131.7, 148.9, 183.6 (C_6H_4). IR (KBr, Nujol, cm^{-1}): 1478, 1111, 1073, 1015, 1006, 876, 840, 796, 734. Anal. Calcd for $C_{43}H_{52}Br_2O_2Zr$: C, 60.63; H, 6.16. Found: C, 60.42; H, 6.25.

$C_{33}H_{42}Br_4GeO_2$ (4). In a Schlenk tube, **3** (0.342 g, 0.40 mmol) was dissolved in 5 mL of dry ether. To this red solution was added $GeBr_4$ (0.160 g, 0.40 mmol) dissolved in 2 mL of ether. After stirring for 14 h at room temperature, the solution color had changed to orange and a light yellow precipitate had formed. The ether was removed in vacuo to give yellow crystals and an orange oil. Extraction with pentane (3 × 5 mL) gave an orange solution containing product and a yellow crystalline residue, which was identified as Cp_2ZrBr_2 by ^{1}H NMR spectroscopy. The orange solution was concentrated to ca. 3 mL and cooled to −40 °C. More Cp_2ZrBr_2 precipitated, and the supernatant was filtered and cooled again to remove yet more Cp_2ZrBr_2. The remaining supernatant was removed, filtered, and dried in vacuo to give **4** (0.318 g, 92%) as an orange oil containing a very small amount of Cp_2ZrBr_2. ^{1}H NMR (300 MHz, C_6D_6): δ 0.849 (t, J = 7.14, 6 H, CH_3), 1.12−1.34, 1.40−1.51 (m, 16 H, CH_2), 2.63 (s, 4 H, CH_2), 3.15 (s, 4 H, OCH_2), 3.20 (t, J = 6.43, 4 H, OCH_2), 7.21 (d, J = 6.62, 4 H, C_6H_4), 7.44 (d, J = 6.63, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 14.2 (CH_3), 23.0, 26.2, 29.5, 29.8, 31.9, 37.6 (CH_2), 49.1 ($C(CH_2)_4$), 71.7, 73.6 (OCH_2), 122.3, 126.7, 130.0, 132.2, 134.0, 152.2 (C_6H_4 and GeC_4). IR (neat, KBr, cm^{-1}): 2954, 2930, 2857, 1486, 1465, 1395, 1111, 1076, 1007, 822, 676. Anal. Calcd for $C_{33}H_{42}Br_4GeO_2$: C, 45.93; H, 4.91. Found: C, 45.68; H, 4.73.

$C_{35}H_{48}Br_2GeO_2$ (5). In a Schlenk tube, **4** (0.35 g, 0.41 mmol) was dissolved in 5 mL of Et_2O, and the reaction mixture was cooled to −78 °C. A fresh solution of 1.4 M MeLi in Et_2O (0.59 mL, 0.82 mmol) was added to the orange solution of **4**. The color changed slowly from orange to yellow upon warming to room temperature over 30 min. A small amount of LiBr precipitated, and after the mixture was stirred for an additional 30 min the solvent was removed to give a cloudy yellow oil. This material was washed with dry pentane and dried in vacuo to give a bright yellow powder. Extraction with benzene produced a yellow solution, which was separated from the white LiBr residue by filtration. The benzene was removed in vacuo, leaving **5** (0.24 g, 63%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65 (s, 6 H, $GeCH_3$), 0.87 (t, J = 6.9, 6 H, CH_3), 1.25 (m, 12 H, CH_2), 1.52 (m, 4 H, CH_2), 2.64 (s, 4 H, CH_2), 3.32 (s, 4 H, OCH_2), 3.39 (t, J = 6.6, 4 H, OCH_2), 7.19 (d, J = 8.4, 4 H, C_6H_4), 7.44 (d, J = 8.4, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −0.8 ($GeCH_3$), 14.0 (CH_3), 22.6, 25.8, 29.5, 31.6, 36.2, 50.0 ($C(CH_2)_4$), 71.5, 73.6 (OCH_2), 119.5, 129.4, 131.6, 134.7, 138.9, 155.4 (C_6H_4 and C_4Ge). IR (neat, KBr, cm^{-1}): 2954, 2929, 2857, 1485, 1465 (sh), 1384, 1111, 1076, 1007, 823. HRMS (EI) Calcd. for $C_{35}H_{48}Br_2GeO_2$: 732.1239. Found: 732.1231.

$C_{21}H_{22}Ge$ (6). A 250 mL Schlenk flask was charged with Cp_2ZrCl_2 (1.6 g, 5.4 mmol) and 100 mL of dry THF. The solution was cooled to − 78 °C in a dry ice acetone bath, and ^{n}BuLi (6.6 mL, 1.6 M, 10.6 mmol) was added dropwise over 5 min. The solution was allowed to stir for 15 min at −78 °C, and then 1,7-diphenyl-1,6-heptadiyne (1.3 g, 5.3 mmol) in 10 mL of dry THF was slowly added over 5 min. The zirconocyclopentadiene was not isolated, but was converted directly to **6** by addition of $GeBr_4$ (2.3 g, 5.9 mmol) at 0 °C. The reaction mixture was allowed to stir for 24 h at room temperature and was then cooled to −78 °C, and MeLi (7.7 mL, 1.43 M) was added dropwise over 5 min. The solution was allowed to slowly warm to room temperature over 3 h and was then stirred for 1 h at room temperature. Pentane (100 mL) was added to the reaction mixture, and the resulting mixture was washed with dilute HCl (75 mL, 0.5 M), H_2O (75 mL), dilute $NaHCO_3$ (75 mL, 1.0 M), and H_2O (75 mL). The organic layer was dried with Na_2SO_4, and the solvent was removed by rotoevaporation to yield the crude product, which was purified by column chromatography (5% EtOAc in hexanes). This yielded **6** (31%, 0.6 g) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70 (s, 6 H, $GeCH_3$), 2.07 (quint, J = 5.4, 2 H, CH_2), 2.74 (t, J = 5.4, 4 H, CH_2), 7.19 (m, 4 H, C_6H_5), 7.35 (m, 6 H, C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −0.7 ($GeCH_3$), 27.5, 30.7 (CH_2), 125.7, 128.8, 128.5, 134.5, 140.3, 156.2 (C_6H_5 and C_4Ge). IR (KBr, cm^{-1}): 3045, 2957, 1592, 1487, 1439, 1079, 826, 764, 694, 599, 574. Anal. Calcd for $C_{21}H_{22}Ge$: C, 72.67; H, 6.40. Found: C, 72.29; H, 6.56. HRMS (EI): Calcd for $C_{21}H_{22}Ge$: 348.0938. Found: 348.0939.

Polymers 7a,b. A 100 mL Schlenk flask was charged with $NiCl_2$ (0.005 g, 0.04 mmol), Zn dust (0.40 g, 6.1 mmol), Ph_3P (0.30 g, 1.1 mmol), bipyridine (0.008 g, 0.05 mmol), and 5.0 mL of DMAc (dimethylacetamide). The mixture was heated to 70 °C in an oil bath for 20 min, resulting in the formation of a red/brown solution indicating the formation of the active Ni catalyst. Compound **2** (0.90 g, 1.5 mmol) in 2.5 mL of dry DMAc was then added dropwise. The reaction mixture was allowed to stir for 3 days at 70 °C and was then poured into 200 mL of rapidly stirring MeOH to precipitate the polymer. The polymer was redissolved in 10 mL of THF. Filtration removed the unreacted zinc, and the polymer was reprecipitated with 200 mL of MeOH. This yielded **7b** (31%, 0.25 g) as a bright yellow powder and a yellow supernatant solution from which the oligomer fraction **7a** was isolated by removal of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.71−0.77 (m, 6 H, $GeCH_3$), 0.87 (br, 6 H, CH_3), 1.27 (br, 12 H, CH_2), 1.55 (br, 4 H, CH_2), 2.72−2.78 (m, 4 H, CH_2), 3.35−3.42 (br m, 8 H, OCH_2), 7.45 (br, 4 H, C_6H_4), 7.61 (br, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −0.40 ($GeCH_3$), 14.1 (CH_3), 22.7, 25.9, 29.5, 31.7, 36.7 (CH_2), 71.6, 73.8 (OCH_2), 126.8, 128.6 (C_6H_4). IR (KBr, cm^{-1}): 2954, 2928, 2855, 1597, 1490, 1465, 1110, 821. Anal. Calcd for $C_{35}H_{48}GeO_2$: C, 73.30; H, 8.45. Found: C, 71.49; H, 8.59.

Polymer 7c. A 250 mL Schlenk tube was charged with Ni(COD)$_2$ (0.14 g, 0.51 mmol) and bipyridine (0.08 g, 0.51 mmol). DMF (10 mL) and toluene (5 mL) were added. A deep blue solution resulted, which was shielded from light with Al foil and heated at 60 °C for 20 min. To this mixture was added **5** (0.30 g, 0.43 mmol) all at once via a gastight syringe as a toluene solution (10 mL). A color change to red was observed, and the mixture was stirred under nitrogen in the dark for 3 h. At this point small, bright yellow droplets of the product polymer formed on the walls of the reaction vessel. Wet THF (20 mL) was promptly added to stop the reaction and dissolve the portion of the product that had precipitated. The red-yellow mixture was poured into a rapidly stirred solution (100 mL) of 0.06 M HCl in MeOH. The bright yellow polymer that precipitated was collected by centrifugation and washed with neutral MeOH (2 × 40 mL). The polymer was dried in air and then swelled with 2 mL of THF. After addition of 10 mL of $CHCl_3$ and heating at 45 °C for 2 days, the entire polymer sample dissolved. The fluorescent yellow solution was filtered and poured into 100 mL of MeOH to reprecipitate the polymer. After washing with MeOH (2 × 40 mL), the bright yellow solid was dried in vacuo to give a yellow powder (0.21 g, 0.39 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77 (m, 6 H, $GeCH_3$), 0.87 (br, 6 H, CH_3), 1.27 (br, 12 H, CH_2), 1.55 (br, 4 H, CH_2), 2.72−2.78 (br m4 H,, CH_2), 3.35−3.42 (br m, 8 H, OCH_2), 7.45 (br, 4 H, C_6H_4), 7.61 (br, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$): δ −0.40 ($GeCH_3$), 14.1 (CH_3), 22.6, 25.8, 29.5, 31.7, 36.7 (CH_2), 50.0 (CC_4), 71.5, 73.8 (OCH_2), 126.8, 128.5, 135.3, 137.9, 139.0, 155.0 (GeC_4 and C_6H_4). IR (KBr, cm^{-1}): 3023, 2953, 2928, 2853, 1598, 1490, 1465, 1365, 1232, 1107, 1001, 819, 791, 723, 576. Anal. Calcd for $C_{35}H_{48}GeO_2$: C, 73.30; H, 8.44. Found: C, 73.06; H, 8.45.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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