From Branched Polyphenylenes to Graphite Ribbons

Jishan Wu,[†] Lileta Gherghel,[†] Mark D. Watson,[†] Jixue Li,[‡] Zhaohui Wang,[†] Christopher D. Simpson,[†] Ute Kolb,[‡] and Klaus Müllen^{*,†}

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany, and Institute of Physical Chemistry, Johannes Gutenberg Universität, D-55128, Mainz, Germany

Received October 25, 2002; Revised Manuscript Received June 16, 2003

ABSTRACT: This article presents the synthesis of graphitic nanoribbons (~ 1 nm wide), containing extended conjugated all-benzenoid segments. These were obtained by intramolecular oxidative cyclodehydrogenation of soluble branched polyphenylenes $\mathbf{6}$, which were prepared by repetitive Diels-Alder cycloaddition of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (1) and diethynylterphenyl (5) in good yield. While insolubility of the obtained graphite ribbons 7 precluded standard spectroscopic structure elucidation, the electronic and vibrational properties were probed by solid-state UV–vis, Raman, and infrared spectroscopy. A wide and unstructured absorption band covering the visible range of the electronic spectrum ($\lambda_{max} \sim 800$ nm) is observed, confirming the highly extended conjugated framework. The structure proof of the ribbon-type polymer is supported by the inclusion of appropriate model compounds. The profile of the visible Raman spectrum of the material is similar to that of a discrete polycyclic aromatic hydrocarbon (PAH) C222H42, characterized by two strong bands (at 1603 and 1322 cm⁻¹), corresponding to the G and D bands of graphite. The obtained graphite ribbons are not linear but rather contain "kinks" due to the structural design of the polyphenylene precursor. High-resolution transmission electron microscopy (HRTEM) images of the graphite ribbons 7 disclose two different domains: one is an ordered graphite layer structure with a layer distance of ca. 3.8 Å, and one is disordered due to the existence of "kinks" in the obtained polymers and/or random stacking of graphite ribbons. Attempts to make linear analogues are so far unsuccessful, emphasizing the critical importance of the geometry of the polyphenylene scaffold to successful oxidative cyclodehydrogenation.

Introduction

Ladder or ribbon-type polymers possessing twodimensionally planar conformation, high electron delocalization, and functional optic-electronic properties attract great scientific interest considering their potential applications in areas such as electroluminescence, plastic lasers, and molecular electronics.¹ The synthesis and characterization of such materials is an ongoing challenge in synthetic chemistry, with only sparse examples of defect-free, soluble hydrocarbon ribbon polymers.^{1b,f} As an allotrope of diamond, fullerenes, and carbon nanotubes, graphite has only sp² hybridized carbons forming planar sheets with high electronic conductivity. Discrete nanoscale two-dimensional graphite subunits with different shapes and sizes have been prepared in our group.² The synthetic route involves two key steps: (i) synthesis of three-dimensional branched oligophenylenes by repetitive Diels-Alder cycloaddition of tetraphenylcyclopentadienones with arylethynylenes or by cobalt-catalyzed cyclotrimerization of diarylethynylenes; (ii) oxidative cyclodehydrogenation of the obtained three-dimensional polyphenylene precursors with $FeCl_3$ or $Cu(OTf)_2 - AlCl_3$ to give two-dimensional graphite segments in high yield. When peripherally substituted, these graphite segments self-assemble to columnar liquid crystalline superstructures. These have demonstrated high one-dimensional charge carrier mobility,²ⁱ promising for organic semiconductors in fieldeffect transistors (FETs) and photovoltaic cells.^{2c} A homologous series of discrete graphite nanosheets (Chart 1) were synthesized, each molecule by a different mul-

Chart 1. Linear Homologous Series of Graphite Ribbon



tistep procedure.^{2a} In analogy to the study of an effective conjugation length in conjugated polymers,³ the electronic absorption maximum red-shifted with molecular aspect ratio due to the ever-increasing delocalized π -surface. This fits into a larger study^{2a,r} of discrete allbenzenoid PAHs, in which excellent correlation was found between the lowest energy absorption band and the size of the aromatic graphitic sheet, regardless of molecular shape. An obvious extension of this work, oxidative planarization of discrete polyphenylenes, to polydisperse, high molecular weight linear species is reported here. We describe the synthesis and characterization of the first ribbonlike graphite framework from branched polyphenylenes by oxidative cyclodehydrogenation.

Results and Discussion

Synthesis. The molecular design of branched polyphenylenes suitable for full cyclodehydrogenation is a

^{*} Corresponding author. E-mail: muellen@mpip-mainz.mpg.de.

[†] Max Planck Institute for Polymer Research.

[‡] Johannes Gutenberg Universität.

Scheme 1. Reported Diels-Alder Cycloaddition Route to Branched Polyphenylenes



critical step to make 2-D graphite ribbons with extended conjugation. In our previous work, repetitive Diels–Alder cycloaddition of bis(tetraphenylcyclopentadienoneyl)benzene (1) and 1,4-diethynylbenzene resulted in high molecular weight branched polyphenylenes as shown in Scheme 1.⁴ As the [4 + 2] cycloaddition between asymmetrically substituted teraphenylcyclopentadienone and monosubstituted acetylene always gives two structural isomers, the cycloaddition product between 1 and 1,4-diethynylbenzene contains three structural isomeric repeat units. Rotation about phen-

yl-phenyl single bonds along the main chain further complicates the conformation. The obtained branched polyphenylenes after cycloaddition as shown in Scheme 1 also contains gaps, i.e., spaces where there are no phenyl rings between the repeat units, which rules out the possibility to obtain a continuous ribbon structure with regular width after planarization. Intramolecular oxidative cyclodehydrogenation yielded only partial planarization, with incoherent and relatively small polycyclic aromatic hydrocarbon (PAH) segments along the polymer backbone.

We report here that replacement of 1,4-diethynylbenzenes with 1,4-diethynyl-2,5-di(4'-tert-butylphenyl)benzenes (5) in the Diels-Alder polymerization produces branched polyphenylene frameworks which can be planarized over much greater length scale. As shown in Scheme 2, selective Suzuki coupling⁵ between 1,4dibromo-2,5-diiodobenzene (2)⁶ and commercially available 4-tert-butylbenzoboronic acid successfully gave the dibromoterphenylene 3 in 92% yield. 1,4-Bis(trimethylsilylethynyl)-2,5-bis(4'-tert-butylphenyl)benzene (4) was then prepared by standard Hagihara-Sonogashira coupling⁷ of **3** with trimethylsilylacetylene in 89% yield. Desilylation of 4 under basic conditions afforded the diethynylterphenylene 5 in 92% yield. Diels-Alder polymerization between compound $\mathbf{\tilde{5}}$ and $\mathbf{1}$ in refluxing diphenyl ether gave the branched polyphenylenes 6, which are soluble in common solvents such as dichloromethane and THF, facilitating structural character-



^{*a*} Key: (a) Pd(PPh₃)₄, K₂CO₃, toluene, 95 °C, 92%; (b) trimethylsilyl acetylene, Pd(PPh₃)₄, CuI, piperidine, 80 °C, 89%; (c) K₂CO₃, methanol/dichloromethane, 92%; (d) Ph₂O, refluxing, 88%; (e) FeCl₃, nitromethane/dichloromethane, 24 h.

Scheme 3^a



^a Key: (a) Ph₂O, reflux; (b) FeCl₃, CH₂Cl₂, CH₃NO₂, 20 h.

ization. ¹H NMR spectra show a broad peak from 7.5 to 6.4 ppm, assigned to the aryl protons, and a single peak at 1.28 ppm assigned to the tert-butyl side groups. A matrix-assisted laser desorption ionization mass spectrum (MALDI-MS) of the polymer consists of a series of peaks up to 10 000 with nominal masses corresponding to integer multiples of the repeating structure. Sizeexclusion chromatography (SEC) with polystyrene standards indicated a number-average molecular weight, $M_{\rm n}=2.5 imes10^4$ ($M_{
m w}/M_{
m n}=2.5$). It should be noted that the actual molecular weight is generally overestimated by SEC when comparing more rigid polymers to polystyrene coils. As previously mentioned, structural isomers must also exist in polymer 6 after the Diels-Alder cycloaddition polymerization. As depicted in Scheme 2, three isomeric polymeric units are possible; i.e., the "head" and "tail" bonds in each repeat unit could be on the same line ("linear"), 120° crossing angle ("cis") or antiparallel ("trans"). All "gaps", which were present in the precursor polymer from our previous work (Scheme 1), are now filled. Conformation isomers arising from rotation along the backbone to give structures not like those depicted could also exist, but they could not be locked into the final planarized ribbon due to overlapping phenyl rings. The last step toward the graphite ribbon 7 is cyclodehydrogenation of precursor 6 with FeCl₃ in nitromethane and dichloromethane. The reaction was quenched after 24 h with methanol, and the black precipitate was washed repeatedly with methanol. The powder was stirred in concentrated hydrochloridic acid for 24 h to remove residual iron compounds and further purified by stirring in hydrazine for 1 day to reduce persisting radical cations. The final product was a black, insoluble powder, graphitelike in appearance.

The feasibility of a high yielding fusion of the precursor polymer **6** to graphite ribbons finds support in the successful conversion of polyphenylene precursors of ever-increasing size to well-defined disks or ribbon-type graphite segments,^{2,9} a relevant example of which is shown in Scheme 3. The Diels-Alder cycloaddition of **1** with 2 equiv of 1-ethynyl-2,3,4,5-tetraphenylbenzenes **(8)** 2e gave three structural isomers **9a**-**c**, which were distinguished by high performance liquid chromatography (HPLC) as three peaks while inseparable by



Figure 1. MALDI MS spectrum for $C_{114}H_{34}$: calculated, 1403.54; found, 1403.30 (100%). Isotope distribution is in good agreement with the simulated results (black bar). In addition, some chloronation took place during the cyclodehydrogenation with Lewis acid iron(III) chloride.

standard column chromatography. The isomer mixture **9a-c** was fused with iron(III) chloride under similar cyclodehydrogenation conditions to give $C_{114}H_{34}$ graphite segments in quantitative yield. The MALDI mass spectrum of the obtained product is shown in Figure 1 and indicates a quantitative dehydrogenation process. The ribbon-type graphite segments $C_{114}H_{34}$ have a similar structure to that of polymer 7 and thus can be considered as a model compound of the graphite ribbons 7.

Characterization of the Graphite Ribbons 7. The poor solubility of the graphite ribbons 7 limits the role of conventional techniques in structure elucidation. Alternatively, infrared, solid-state Raman and UV–vis spectroscopy are standard tools for the characterization of insoluble PAHs and nanosized graphite domains. The optical characterization of the product was achieved by UV–vis spectroscopy of a thin film, prepared mechanically by simply smearing samples on a quartz substrate. As shown in Figure 2, a broad absorption, with a continuum-like appearance in the visible range and an approximate maximum of 800 nm was observed. This



Figure 2. Solid-state UV-vis spectrum of graphite ribbon 7, C114H34, and C222.

broad and unstructured profile is similar to that observed for a recently reported²ⁿ giant PAH with 222 carbon atoms (C₂₂₂), included in Figure 2 for comparison. This compound, so far the largest discrete all benzenoid PAH, contains 37 so-called "full" aromatic rings. According to the π -sextet model of Armitt and Robinson, which was subsequently further developed by Clar, the π electrons of the all benzenoid hydrocarbons tend to group into disjoint sextets, which coincide with isolated "full" benzene rings.^{20,p,q} These rings, marked with the Robinson circle, are connected together by C–C single bonds. Therefore, some benzene rings are viewed as the seat of π -sextets, some as "empty". As described in the Introduction, there is excellent correlation between the optical spectra of all-benzenoid PAHs and their size with little influence of the shape of the molecules. Because of its similar graphite-related model structure and its size, C_{222} can be used as a model for the optical characterization of graphite ribbons.^{2a,r} The UV-vis spectrum of C₂₂₂ showed an absorption over the complete visible range of the electronic spectrum, with a maximum of the band at approximately 765 nm.²ⁿ The similarity between the UV-vis spectra of these two systems suggests that the extended ribbon segments within polymer 7 consist of at least 200 carbons (Figure 2). On the other hand, the model compound $C_{114}H_{34}$ shows a continuum-like absorption with an approximate maximum of 675 nm (Figure 2). The red shift of the absorption band in the polymer 7 compared to this model compound also suggests a higher conjugation in the graphite ribbons 7.

Relevant information about the polymer 7 has been obtained by comparison of the most characteristic spectroscopic features of the infrared spectrum of the branched polyphenylene precursor 6 and that of the cyclodehydrogenated product 7. It has to be pointed out that while the vibrational spectrum of 6 exhibited strong absorptions the vibrational spectrum of 7 showed only weak peaks, thus indicating that the final product has reached a sizable dimension and complexity. Of particular diagnostic importance are the traditional group frequencies normally used in spectroscopic analysis of monosubstituted benzene rings (at 698, 750, and around 3060 cm^{-1}) and the combination peak at 4050 cm^{-1} . The last is characteristic of the "free" rotating benzene rings and can indicate the existence of non condensed benzene rings in the molecule.¹⁰ All these bands were observed in the spectrum of the branched polyphenylene precursor 6, but have disappeared in the spectrum of the cyclodehydrogenated product 7 (Figure 3). A new set of



Figure 3. Infrared spectra of branched polyphenylene precursor **6** (solid line) and graphite ribbon **7** (dot line).



Figure 4. Raman spectra of graphite ribbon 7, C114H34, and C222.

weak bands in the spectral region related to C–H outof-plane motion suggests the formation of multiply substituted benzene rings and of complete fused aromatic rings.

The successful application of Raman spectroscopy to the determination of extended π -conjugation and ordering of cyclodehydrogenated products has been demonstrated and is utilized here in a similar fashion.⁴ Spectra were recorded from solid samples of polymer 7 using 514 nm excitation laser wavelength. The first-order Raman spectrum was characterized by two relevant signature features, a first band situated at 1322 cm⁻¹, with a shoulder at 1254 cm⁻¹ and a second band located at 1603 cm⁻¹ (Figure 4). The investigations of vibronic frequencies and Raman intensities of several all-benzenoid PAHs of different, but well-defined structure and size revealed as common features a line near 1600 cm⁻¹ and two or more lines near 1300 cm⁻¹.¹¹ The number of the peaks in the region around 1300 cm⁻¹, their relative intensities, and positions changed according to the size and the symmetry of the molecules. On the other hand, the Raman spectra of polymer 7, the model compound C₁₁₄H₃₄ and very large PAHs as C₂₂₂ could be correlated, on analytic grounds, to those observed in graphitic materials with different degree of crystalline order, socalled disordered graphite. These materials exhibit some defects which break the conjugation of the ideal, highly crystalline, two-dimensional graphite lattice and lead to the formation of nanosized graphitic islands. Two Raman peaks at 1580 and 1330 cm^{-1} appear in the spectrum of disordered graphite, usually referred to as the G and the D bands, respectively. The first band (G) is the only feature observed in the first-order Raman spectrum of highly ordered, crystalline graphite. The D



Figure 5. (A) (a) TEM images of the graphite ribbon samples **7**, where an ordered graphite layer structure is marked by a square; (b) high-resolution image (HRTEM) of marked area exhibiting a layer distance of 3.8 Å; (c) selected area electron diffraction (SAED) pattern from marked area showing 002 reflections. (B) Another extended highly ordered graphite layer structure.

peak originates from imperfections and small conjugated domains with finite size. Given the similarity of the expected structure of the graphite ribbon reported here with "nanocrystalline" or disordered graphite and all-benzenoid PAHs, the line centered at 1603 cm⁻¹ could be assigned to the G band and the lines located around 1322 and 1254 cm⁻¹ to the D bands. Structural defects of the obtained graphite ribbons,

Structural defects of the obtained graphite ribbons, arising from the incomplete cyclodehydrogenation, could contribute to the width of the D band. The broadening of this band is correlated to the convolution of the Raman transitions from a distribution of aromatic "domains" with different structures and dimension. For disordered graphite, the ratio of the intensities of the D and G peaks [I(D)/I(G)] varies inversely with L_a and the number of ordered aromatic rings, according to¹²

$I(D)/I(G) = C(\lambda)/L_a$

where L_a is the molecule diameter or in-plane correlation length and $C(\lambda)$ is a parameter dependent on excitation laser wavelength (for $\lambda = 514$ nm, $C(\lambda) \sim 44$ Å). This relation yields $L_a = 6.2$ nm, corresponding to ribbon segments with ~42 conjugated "full" aromatic rings along the polymer main chain. These results and the similarity to the Raman spectrum of C₂₂₂ (Figure 4) support the upper size of the aromatic π -system determined by the absorption maximum from UV–vis spectroscopy. Compared with polymer 7 and C₂₂₂, the model compound C₁₁₄H₃₄ has a similar Raman spectrum with a better-resolved D band and the relative intensity of D band to that of G band is higher. These features are ascribed to the smaller conjugated size in the model compounds.

The morphology of the obtained graphite ribbon samples was probed by high-resolution transmission electron microscopy (HRTEM) (Figure 5). In the larger areas, disordered graphite structure was observed. However, an ordered graphite layer structure surrounded by amorphous regions was also found. A typical example shown in Figure 5A discloses an ordered graphite structure which extends approximately over 6.5 nm width and 35 nm length. Selected area electron diffraction (SAED) on this region reveals a layer distance of 3.8 Å, which is larger than that of crystalline graphite (3.45 Å). Considering the existence of bulky

tert-butyl side groups as well as the "kink" structures in the polymer 7, this larger distance appears reasonable. Another kind of graphite layer structure over tens of nm to μ m was also observed in some areas as shown in Figure 5B. These ordered structures obviously arise from the ordered stacking of linear graphite ribbons. Direct observation of single graphite molecules is unlikely because of their strong aggregation. The appearance of the large disordered areas could be the consequence of random stacking of the insoluble graphite materials during the precipitation from solution and/ or the existence of "kink" microstructures in the polymer chain. We should point out that, as we found in previous work,² structural defects arising from incomplete cyclodehydrogenation can occur, especially when preparing insoluble giant graphite segments. Here, the structural defects could also exist and full structural proof is impossible due to the very poor solubility of polymer 7.

Attempt toward Linear Graphite Ribbons. Efforts to make precursor polymers (Scheme 4) like polyterphenylenes (10) or branched polyphenylenes (12) by Yamamoto coupling¹³ of compound **3** or Suzuki coupling between 1,4-dibromo-2,3,5,6-tetrabenzene (11) and 1,4-benzenediboronic acid all failed most likely because of severe steric hindrance arising from the phenyl-phenyl repulsion. To minimize the steric problem, we designed an alternative route in which a terphenyl could be copolymerized with an unhindered monomer. 1,4-Dibromo-2,5-di(2'-biphenyl)ylbenzene (13) was prepared by selective Suzuki coupling between 1 and 2-biphenylboronic acid in 77% yield. Compared with 11, compound 13 has two biphenyl substituents with high rotational freedom, and its reactive sites are less hindered. Polymerization of 13 with 1,4-benzenediboronic acid under standard Suzuki coupling conditions only gave oligomers detected by MALDI-MS. The low molecular weight could be ascribed to the poor solubility of the product as well as to, albeit reduced, steric hindrance during the reaction. The oxidative cyclodehydrogenation of the oligomers 14 was also attempted with excess FeCl₃ in the mixed solvent dichloromethane/ CS₂; however, only partially fused and chlorinated products instead of ribbon oligomer 15 were observed from MALDI-MS. This prompted a model study to check the reactivity of the new polyphenylene scaffolding present in the repeating units of precursor 14. The



^{*a*} Key: (a) Ni(COD)₂, bipyridine, COD, toluene/DMF, 80 °C; (b) 1,4-benzenediboronic acid, Pd(PPh₃)₄, K₂CO₃, 95 °C; (c) Pd(PPh₃)₄, K₂CO₃, 95 °C, 77%; (d) 4-*tert*-butylbenzoboronic acid, Pd(PPh₃)₄, K₂CO₃, 75 °C, 75%; (e) FeCl₃, nitromethane/DCM.

model compound 16 was prepared by similar Suzuki coupling between 13 and excess 4-tert-butylbenzoboronic acid in 75% yield. Attempted cyclodehydrogenations of **16** with FeCl₃, Cu(OTf)₂-AlCl₃, or SbCl₅ all gave a complicated mixture but not the desired hexabenzocoronene derivative 17. As we have reported,^{2k} hexaphenylbenzenes can be easily fused to hexabenzocoronenes under the same cyclodehydrogenation conditions. The success of the reaction is acutely dependent on the nature of substituents attached at the periphery, that is electron-withdrawing or electron-donating power. The difference of compound 16 from the hexaphenylbenzenes lies only in the position of the single bonds, which serve to hold the benzene rings in a scaffold for planarization. Higher conformational freedom, e.g., where the biphenyl group can twist out of the plane of the center phenyl ring, could impede the planarization. At the same time, the less symmetrical structure of 16 could promote selective radical formation with reduced reactivity, thus giving only partially fused product.

Conclusion

By rational synthetic design, branched polyphenylenes **6** prepared by repetitive Diels-Alder cycloaddition could be transformed into graphitelike ribbons under oxidative cyclodehydrogenation conditions. The obtained materials were most likely not structurally linear; however, they gave the first case of twodimensional highly conjugated graphite structures with high aspect ratio. Estimations of the extent of conjugation by UV-vis and Raman spectroscopy find excellent

correlation. Particularly interesting is their formal similarity with disordered graphite, which can provide further information as to their structural and spectroscopic properties. The HRTEM measurement gave a direct observation of this ribbonlike polymer. In this context, the 2-D ribbon-type polymers reported here could be used as models for polydisperse nanosized graphitic domains in several disordered carbon materials. Efforts to make isomer-free precursors for linear graphite ribbons by Yamamoto or Suzuki coupling reaction were precluded by steric hindrance, a problem that will often be encountered when making extended ribbons. This problem can be alleviated somewhat by copolymerization of monomers which define the width, along with a nonsterically hindered monomer. However, an oligophenylene precursor obtained in this way failed to undergo planarization under our cyclodehydrogenation conditions, revealing the strong dependence of this reaction on subtleties. In any case, a successful precursor route to graphite ribbons paves the way to novel carbon-rich ribbonlike nanomaterials, which could be further studied by surface characterization tools such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc. Poor solubility brings practical processing difficulties, and our next steps will include investigations of the cyclodehydrogenation on a metal surface by heat treatment¹⁴ or other oxidants. Postsynthesis noncovalent modification of rigid molecules is becoming a proven way of engineering processability and self-assembly,¹⁵ even in the case of inorganic nanocrystals.¹⁶ In this light, we shall prepare ribbon structures with pendant functionality that can act as a handle for noncovalent attachment of processing aids.

Experimental Section

General Information. Except where noted, all starting materials were purchased from Aldrich, Acros, and ABCR and used as received. ¹H NMR and ¹³C NMR spectra were recorded in CD_2Cl_2 , and $C_2D_2Cl_4$ on a Bruker DPX 250 spectrometer and referenced to residual proton solvent. MALDI TOF mass spectra were obtained with TCNQ as matrix according to the reported sample-preparing method.¹⁷ The optical absorption measurements were performed at ambient temperature on a quartz substrate with a UV/vis/NIR Perkin-Elmer Lambda 900 spectrometer. IR spectroscopy was performed on transmission using a Nicolet FT-IR 730 spectrometer. Raman spectra were examined in KBr pellets and recorded on a Dilor XY 800 spectrometer with a liquid-nitrogen cooled CCD detector and Raman microscopically unit. As excitation source Ar⁺ laser has been used. Powder wide-angle X-ray diffraction (WAXD) experiments were performed using a Siemens D 500 Kristalloflex with graphite-monochromatized Cu Ka X-ray beam, emitting from a rotating Rigaku RV-300 anode. SEC measurement was done in THF with polystyrene as standard and UV Soma S-3702 as detector. Elemental analyses were performed at the Institute of Organic Chemistry, Johannes-Gutenberg University, Mainz, Germany. Melting points were measured on Büchi B-545 with a gradient rate of 2 °C/min. HRTEM measurements were done on a Philips Tecnai F30 analytical TEM instrument, operated at an accelerating voltage of 300 kv.

Synthesis. 1,4-Dibromo-2,5-di(4'-tert-butylphenyl)benzene (3). The mixture of 11.2 g of 1,4-dibromo-2,5-diiodobenzene (2) (22.98 mmol), 9.0 g of 4-tert-butylbenzoboronic acid, 795 mg of Pd (PPh₃)₄, and 31.71 g of K₂CO₃ in 230 mLof toluene and 115 mL of water was deoxygenated by two "freeze-pumpthaw" cycles and heated to 95 °C for 18 h. After cooling, the mixture was extracted with 100 mL toluene. The organic layer was washed with water three times, dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE) to give 10.6 g of pure product as white crystals (92%). Mp: 264.4 °C. FD-MS (8 keV): 500.2 (M⁺). ¹H NMR (CD₂-Cl₂, 250 MHz): δ , ppm 7.64 (s, 2H), 7.49 (d, J = 8.2 Hz, 4H), 7.39 (d, J = 8.2 Hz, 4H), 1.37 (s, 18H). ¹³C NMR (CD₂Cl₂, 125 MHz): δ, ppm 151.6, 142.9, 136.9, 135.7, 129.3, 125.5, 121.6, 34.9, 31.5. Anal. Calcd for C₂₆H₂₈Br₂: C, 62.42; H, 5.64. Found: C, 62.40; H, 5.61.

1,4-Di(4'-tert-butylphenyl)-2,5-di(trimethylsilylethynyl)benzene (4). A 4.0 g sample of 3 (0.08 mmol), 277 mg of Pd-(PPh₃)₄, and 150 mg of copper(I) iodide in 30 mL of piperidine were deoxygenated by sparging with argon for 20 min, and then 2.36 g of trimethylsilylacetylene (24 mmol) was added. The mixture was heated to reflux under argon overnight. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/DCM = 10:1) to give 3.8 g of pure product as a white powder (89%). Mp: 211.7 °C. FD-MS (8 keV): 534.92 (M⁺). ¹H NMR (CD₂-Cl₂, 250 MHz): δ , ppm 7.60 (d, J = 8.5 Hz, 4H), 7.58 (s, 2H), 7.46 (d, J = 8.5 Hz, 4H), 1.37 (s, 18H, *tert*-butyl), 0.14 (s, 18H, TMS). ¹³C NMR (CD₂Cl₂, 125 MHz): δ, ppm 151.3, 142.7, 136.4, 134.3, 129.2, 125.2, 122.1, 104.7, 99.8, 34.8, 31.4. Anal. Calcd for C₃₆H₄₆Si₂: C, 80.83; H, 8.67. Found: C, 80.81; H, 8.64

1,4-Diethynyl-2,5-di(4'-*tert*-**butylphenyl)benzene (5).** A 3.1 g sample of **4** (5.8 mmol) was dissolved in 20 mL of DCM and 15 mL of methanol, and then 4.8 g of K_2CO_3 (34.8 mmol) was added. The mixture was vigorously stirred for 3 h at room temperature and poured into 100 mL of water. The mixture was extracted with 50 mL of DCM, and the organic layer was washed with water three times and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, PE/DCM = 10:1) to give 2.08 g of pure product (92%). Mp: 252.6 °C. FD-MS (8 keV): 390.62 (M⁺). ¹H NMR (CD₂Cl₂, 250

MHz): δ , ppm 7.59 (s, 2H), 7.53 (d, J = 8.5 Hz, 4H), 7.38 (d, J = 8.5 Hz, 4H), 3.16 (s, 2H), 1.29 (s, 18H, *tert*-butyl). ¹³C NMR (CD₂Cl₂, 125 MHz): δ , ppm 151.2, 142.4, 135.8, 135.5, 129.0, 125.4, 120.9, 83.3, 82.4, 34.9, 31.7. Anal. Calcd for C₃₀H₃₀: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.73.

Polyphenylene Precursors 6. In a Schlenk tube, 250.0 mg of **5**, 442.2 mg of 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene (**1**), and 5 mL of diphenyl ether were deoxygenated and then heated to reflux under argon for 15 h. After cooling, methanol was added and the precipitate was collected. The crude product was purified by repeated ($3\times$) reprecipitation from THF solution with methanol to give 580 mg of a white powder (88%). ¹H NMR (CD₂Cl₂, 250 MHz): δ , ppm 7.5– 6.4 (br, 43H), 1.28 (s, 18H, *tert*-butyl). ¹³C NMR (CD₂Cl₂, 125 MHz): δ , ppm 149.6, 142.5–124.7 (m), 34.7, 31.5. Anal. Calcd for (C₈₀H_{64)n}: C, 93.71; H, 6.29. Found: C, 93.69; H, 6.30.

Cyclodehydrogenation of Precursor 6 To Give Graphite Ribbon 7. A 205 mg sample of polyphenylene precursor **6** in 100 mL of dichloromethane was deoxygenated by spurging with argon, which was continued throughout the reaction. Then, 4.54 g of iron(III) chloride in 16 mL of degassed nitromethane was added dropwise. The mixture was stirred for 24 h followed by quenching with 100 mL of methanol. The black precipitate was collected and washed with methanol until the filtrate was colorless. The powder was stirred in 6 M HCl for 24 h to remove residual ferrous impurities. The sample was then stirred with 25% hydrazine (aqueous) for 24 h to reduce any persistent radical cations. The powder was collected, washed with water and then methanol, and dried under vacuum to give 185 mg of black powder.

Synthesis of Compounds 9a–c. A solution of ethynyltetraphenylbenzene (**8**, 301.6 mg, 0.742 mmol) and compound **1** (250.0 mg, 0.362 mmol) in diphenyl ether (10 mL) was deoxygenated and heated at reflux under argon atmosphere for 15 h. After cooling, the product was precipitated from ethanol (100 mL), washed by ethanol, and dried under vacuum. Thus, 434.1 mg (83%) of pure compound was obtained. MALDI–MS: m/z = 1447.48; m/z(calculated) = 1447.76 for $C_{114}H_{78}$. ¹H NMR (250 MHz, $C_2D_2Cl_4$): δ , ppm 7.4–6.6, multiplet.

Synthesis of the Model Compound C₁₁₄**H**₃₄. A 50 mg sample of compound **9a**–**c** was dissolved in 40 mL of fresh dichloromethane deoxygenated by bubbling argon for 10 min, and then 739 mg of iron(III) chloride dissolved in 3 mL of nitromethane was added by syringe over 5 min. The reaction was quenched after 20 h by 100 mL of methanol. The black precipitate was washed by methanol and stirred in 25% hydrazine for 24 h. The powder was washed by methanol and dried under vacuum to provide 37 mg product. MALDI–MS: m/z = 1403.296; m/z(calculated) = 1403.54 for C₁₁₄H₃₄.

1,4-Dibromo-2,5-bis(2'-biphenyl)ylbenzene (13). A 3.52 g sample of **2** (7.21 mmol), 3.0 g of 2-biphenylboronic acid (15.2 mmol), 416 mg of Pd(PPh₃)₄, 9.96 g of K₂CO₃ in 140 mL of toluene, and 70 mL of water were degassed by three "freeze–pump–thaw" cycles and heated to reflux overnight. The organic layer was washed with water and dried over magnesium sulfate, then concentrated under reduced pressure and the residue was purified by column chromatography (silica gel, PE/DCM = 10:1) to give 3.0 g of a white powder (77%). Mp: 224.2 °C. FD–MS (8 keV): 540.28 (M⁺). ¹H NMR (CD₂Cl₂, 250 MHz): δ , ppm 7.11–7.53 (br, m). ¹³C NMR (CD₂Cl₂, 125 MHz): δ , ppm 143.2, 141.4, 140.9, 138.5, 135.7, 131.0, 130.5, 129.7, 128.9, 128.3, 127.4, 127.1, 122.5. Anal. Calcd for C₃₀H₂₀-Br₂: C, 66.69; H, 3.73. Found: C, 66.65; H, 3.72.

Oligophenylenes 14. A 500 mg sample of **11**(0.926 mmol), 153.4 mg of *p*-phenyldiboronic acid (0.926 mmol), and 64 mg of Pd(PPh₃)₄ were placed in 20 mL toluene, and then 10 mL of 1 M K₂CO₃(aq) was added. The mixture was degassed by three "freeze–pump–thaw" cycles and then heated to reflux for 48 h. During the reaction, a white precipitate formed because of the poor solubility of the product. After cooling, the solid was collected and the organic layer was poured into 100 mL of methanol to complete the precipitation. The combined crude product was dissolved in THF/CS₂ and reprecipitated with methanol two times. The white powder was washed with

methanol and dried under vacuum to give 320 mg of oligomers 12. ¹H NMR (CD₂Cl₂, 250 MHz): δ , ppm 6.50–8.72 (br, m). ¹³C NMR (CD₂Cl₂, 125 MHz): δ, ppm 140.9, 129.32-122.82 (multi). Anal. C, 94.10; H, 5.12.

1,4-Bis(4'-tert-butylphenyl)-2,5-bis(2'-biphenyl)ylbenzene (16). See synthetic protocol for 13. First 250 mg of 13 (0.463 mmol), 329 mg of 4-tert-butylbenzoronic acid (1.85 mmol), 53.4 mg of Pd(PPh₃)₄, 638.5 mg K₂CO₃ in 6 mL of toluene, and 3 mL of water were heated to 95 °C overnight. After standard workup and column chromatography (silica gel, PE/DCM = 5:1) 227 mg of pure product as white powder was obtained (75%). FD-MS (8 keV): 646.90 (M+). ¹H NMR (CD₂-Cl₂, 250 MHz): δ , ppm 7.49–6.98 (br, 18H), 6.46 (d, J = 8.2Hz, 4H), 6.62 (d, J = 8.2 Hz, 4H), 1.28 (s, 18H). ¹³C NMR (CD₂-Cl₂, 125 MHz): δ , ppm 149.3, 144.9, 141.4, 141.3, 140.2, 139.9, 139.4, 137.8, 133.7, 132.0, 130.2, 129.4, 128.9, 127.8, 127.6, 126.3, 124.8, 34.6, 31.4. Anal. Calcd for C₅₀H₄₆: C, 92.83; H, 7.17. Found: C, 92.80; H, 7.16.

Acknowledgment. We acknowledge financial support from the Zentrum für Multifunktionelle Werkstoffe und Miniaturisierte Funktionseinheiten (BMBF 03N 6500), EU-TMR Project SISITOMAS, the Deutsche Forschungsgemeinschaft (Schwerpunkt Feldeffekt-transistoren), and the EU Project DISCEL (G5RD-CT-2000-00321) and the help from Ms. Hansjög Menges for the Raman spectroscopy measurement.

References and Notes

- (1) (a) Scherf, U. J. Mater. Chem. 1999, 9, 1853-1864. (b) Scherf, U.; Müllen, K. Makromol. Chem. Rapid Commun. 1991, 12, 489. (c) Freund, T.; Scherf, U.; Müllen, K. Macromolecules, 1995, 28, 547. (d) Schlüter, A.; Löffler, M.; Enkelmann, V. *Nature (London)* **1994**, *36*8, 831–834. (e) Sclicke, B.; Schirmer, H.; Schlüter, A. *Adv. Mater.* **1995**, *7*, 544–546. (f) Löffler, M.; Schlüter, A.; Gessler, K.; Saenger, W.; Toussaint, J.; Bredas, J. Angew. Chem., Int. Ed. Engl. **1994**, 33, 2209–2212. Angew. Chem. 1994, 106, 2218. (g) Chmil, K.; Scherf, U. Acta *Polym.* **1997**, *48*, 208. (h) Goldfinger, M. B.; Swager, T. M. J. Am. Chem. Soc. **1994**, *116*, 7895. (i) Tour, J. M.; Lamba, J. S. S. J. Am. Chem. Soc. **1993**, 115, 4935. (j) Tour, J. M.; Lamba, J. S. S. J. Am. Chem. Soc. **1994**, 116, 11723. (k) Tsuda, A.; Osuka, A. Science 2001, 293, 79-82. (l) Tsuda, A.; Osuka, A. *Adv. Mater.* **2002**, *14*, 75–79. (a) Watson, M.; Fechtenbötter, A.; Müllen, K. *Chem. Rev.*
- (2)2001, 101, 1267-1300. (b) Samori, P.; Fechtenkötter, A.; Jäckel, F.; Böhme, T.; Müllen, K.; Rabe, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 11462–11467. (c) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. *Science* **2001**, *293*, 1119–1122. (d) Müller, M.; Kübel, C.; Müllen, K. Chem.-Eur. J. 1998, 4, 2099-2109. (e) Iyer, V. S.; Yoshimura, K.; Enkelmann, V.; Epsch, R.; Rabe, J.; Müllen, K. Angew. Chem., Int. Ed. **1998**, *37*, 2696–2699. Angew. Chem. 1998, 110, 2843-2846. (f) Dötz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Müllen, K. J. Am. Chem. Soc. 2000, 122, 7707-7717. (g) Fechtenbötter, A.; Tchebotareva, N.; Watson, M.; Müllen, K. *Tetrahedron Symp.* **2001**, *57*, 3769–3783. (h) Herwig, P.; Kayser, C.; Müllen, K.; Spiess, H. W. Adv. Mater. 1996, 8, 510–513. (i) van de Craats, A. M.; Warman, J. M.; Fechenbötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. Adv. Mater. **1999**, *11*, 1469-1472. (j) Fechtenbötter, A.; Saalwächter, K.; Harbison, M. A.; Müllen, K.; Spiess, J. W. Angew. Chem., Int. Ed. Engl. **1999**, *38*, 3039–

3042. Angew. Chem. 1999, 111, 3224-3228. (k) Stabel, A.; Herwig, P.; Mullen, K. Angew. Chem. 1995, 107, 335-339. Angew. Chem., Int. Ed. Engl. 1995, 34, 1609-1611. (l) Iyer, V. Š.; Wehmeier, M.; Branď, J. D.; Keegstra, M. A.; Müllen, K. Angew. Chem., Int. Ed. **1997**, *36*, 1604–1607. Angew. Chem. **1997**, *109*, 1676–1679. (m) Müller, M.; Iyer, V. S.; Kübel, C.; Enkelmann, V.; Müllen, K. Angew. Chem. 1997, *109*, 1679–1682. (n) Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Przybilla, L.; Räder, H. J.; Müllen, K. *Chem.*– Eur. J. 2002, 8, 1424-1429. (o) Clar, E. Polycyclic Hydrocarbons; Springer: Berlin, Göttingen, and Heidelberg Germany; Academic Press Inc.: London, 1964; Vols. I and II. (p) Clar, E. The Aromatic Sextet; Wiley: London, 1972. (q) Armitt, J. W.; Robinson, R. J. Chem. Soc. 1925, 1604. (r) Gherghel, L.; Müllen, K. Manuscript in preparation.

- Marting, R. E.; Diederich, F. Angew. Chem., Int. Ed. Engl. 1999, 38, 1350-1377; Angew. Chem. 1999, 111, 1440-1469. (3)
- (a) Shifrina, Z. B.; Averina, M. S.; Rusanov, A. L.; Wagner, M.; Müllen, K. *Macromolecules* **2000**, *33*, 3525–3529. (b) Mukamal, H.; Harris, F. W.; Rakutis, R. O.; Stille, J. K. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 1967, 8, 496. (c) Stille, J. K.; Harris, F. W.; Rakutis, R. O.; Mukamal, H. J. Polym. Sci., Part B **1966**, 4, 791. (d) Stille, J. K.; Rakutis, R. O.; Mukamul, H.; Harris, F. W. Macromolecules 1968, 1, 431. (e) Stille, J. K.; Noren, G. K. J. Polym. Sci., Part B 1969, 7, 525.
- (5) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. Synth. Commun. 1981, 11, 513. (b) Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457
- (6) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. J. Am. Chem. Soc. 1997, 119, 4578–4593.
- Taskahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, (7)N. Synthesis 1980, 627.
- Schumm, J. S.; Pearson, D. L.; Tour, J. M. Angew. Chem., Int. Ed. 1994, 33, 1306; Angew. Chem. 1994, 106, 1445.
- Another model reaction: Diels-Alder reaction between 1,4-(9)diethynyl-2,5-di(4'-dodecylphenyl)benzene (a structure analogous to 5) and 2 equiv of tetra(4-dodecylphenyl)cyclopentadienones provides a soluble branched oligophenylenes, which can be fused to give a soluble, dodecyl-substituted C78 graphite segment (as shown in Chart 1). Simpson, C. D.; Müllen, K.; et al. Manuscript in preparation.
- (10) Jones, R. N. Sandorfy, C. Chemical Applications of Spectroscopy; In *Techniques of organic chemistry*; Weissberger, A., Ed.; Interscience: New York, 1956; Vol. IX.
- (11) (a) Castiglioni, C.; Mapelli, C.; Negri, F.; Zerbi, G. J. Chem. *Phys.* 2001, 114, 963–974. (b) Castiglioni, C.; Negri, F.; Rigolio, M.; Zerbi, G. J. Chem. Phys. 2001, 115, 3769–3778. (c) Negri, F.; Castiglioni, C.; Tommasini, M.; Zerbi, G. J. Phys. Chem. A 2002, 106, 3306–3317. (d) Mapelli, C.; Castiglioni, (C) Agrile K. Phys. Rev. B 1000, 60, 19705. C.; Zerbi, G.; Müllen, K. Phys. Rev. B 1999, 60, 12710-12725. (e) Mapelli, C.; Castiglioni, C.; Meroni, E.; Zerbi, G. *J. Mol. Struct.* **1999**, *481*, 615–620. (f) Rigolio, M.; Castiglioni, C.; Zerbi, G.; Negri, F. J. Mol. Struct. 2001, 563-564, 79-87.
- (12) Ferrari, A. C.; Robertson, J. *Phys. Rev. B* 2000, *61*, 1.
 (13) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. Macromolecules 1992, 25, 1214.
- (14) Weiss, K.; Beernink, G.; Dötz, F.; Birkner, A.; Müllen, K.; Wöll, C. H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3748. (15) Sautter, A.; Thalacker, C.; Würthner, F. *Angew. Chem., Int.*
- Ed. 2001, 40, 4425-28.
- Li, L.-S.; Walda, J.; Manna, L.; Alivisatos, A. P. Nano Lett. (16)**2002**, 2, 557-60.
- (17) Przybilla, L.; Brand, J. D.; Yoshimura, K.; Räder, J.; Müllen, K. Anal. Chem. 2000, 72, 4591.

MA0257752