

Ferrocenyl-polyphenylenes: Toward Metallo-organic Polyaromatics

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This work continues our investigations into substituted polyaromatic hydrocarbons (PAHs). Presented is a new series of ferrocenyl-substituted polyphenylenes and the successful Lewis acidcatalyzed cyclodehydrogenation of one of these to form an eight-ring fused PAH supporting a ferrocene moiety (16-ferrocenyl(tribenzo[e;g,h,i;k])perylene (6)), the largest of its kind. The failure to generate further metallo-organic superaromatics is discussed in relation to the structure of the precursors and the oxidation of the ferrocene metal center. The synthesis of the polyphenylenes involves the [2+4] Diels-Alder reaction of phenyl, ferrocenyl, and hydrogen-terminated ferrocenyl acetylenes and tetraphenylcyclopentadienone. The full spectroscopic characterization and the electronic and redox properties of all the systems are described and compared. The single-crystal X-ray structure of tetraphenyl ferrocenyl benzene (1), the precursor to **6**, is also discussed.

Introduction

Carbon-rich organometallic compounds represent a rapidly growing subfield at the interface of organic and organometallic chemistry. Carbon-rich ligands offer a range of interesting properties including facile electron transfer to (and from) a metal surface. As a result, organometallic fragments assembled on substituted benzenes, polyaromatics, and heteroaromatics, such as pyridine, have attracted considerable interest as potential models for organometallic polymers,¹ as targets for the study of electron-transfer processes, and in the generation of molecular wires.² Indeed in the past decade, the interest in organometallic polymers has increased owing to their application in light-emitting diodes,³ molecular magnets,⁴ gas sensors,⁵ and photovoltaic devices.⁶

Among these systems, ferrocene has found many applications in synthetic organic chemistry and material sciences.⁷ The stable coordination of the cyclopentadienyl ligands, the synthetic ease of functionalization, the possibility of introducing chirality, and the reversible redox behavior of the metal center are attractive features of ferrocene-based molecules.⁸ Examples include ferrocene-mediated electron

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transfer in glucose oxidase and anion, cation, and DNA biosensors.⁹

Ferrocenylacetylenes in particular offer a wide range of potential applications in NLO,¹⁰ in catalysis, and as models of charge transfer, and they are key synthetic building blocks for the generation of more complex molecules with well-defined magnetic¹¹ and electronic properties.¹² Most ferrocene complexes that are investigated for their optical non-linearities comprise ferrocene as donor and -CN- or -CHO-substituted benzene, stilbene, or azobenzene derivatives, as acceptor.¹³

The spacing between the cyclopentadienyl rings in a ferrocenyl moiety is about 3.3 Å, geometrically similar to the interplanar spacing in $\pi - \pi$ stacking arrangements.¹¹ In this regard, ferrocene is particularly suited for incorporation into all-carbon polycyclic and N-doped polycyclic molecules. Polyaromatic hydrocarbons (PAHs) have a number of attributes that could make them useful as linking groups in donor-acceptor organometallic systems. They are planar and relatively rigid with a fixed geometry. Their highly delocalized π -systems with small HOMO-LUMO energy separations and low-energy vacant π^* -orbitals are likely to facilitate electronic communication between donors and acceptors. Surprisingly, although large polycyclic materials incorporating up to 222 carbon atoms have been characterized, very few include an organometallic moiety. Known examples include Bunz's ethynylated cyclobutadienes,14-17

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Scheme 1. Scheme for the Synthesis of Polyphenylenes 1, 2, 3, 4, and 5 (All Synthesized by the Diels-Alder Reaction between Tetraphenylcyclopentadienone and the Appropriate Acetylene) and the Ferrocenyl-Supported PAH 6^a



^{*a*}(i)–(iv) Tetraphenylcyclopentadienone, benzophenone, 200 °C, 48 h; (i) **1** 70%; (ii) **2** 36%; (iii) **3** 44%, **4** 18%; (iv) **5** 75%; (v) AlCl₃/CuCl₂, CS₂, RT, 48 h, **6** 15%.

the incorporation of tricarbonylchromium into an HBC derivative,¹⁸ and an L-shaped 4-(2-ferrocenylvinyl)pyrene compound.¹¹

To broaden the number of molecules of this type in the literature, we devised the synthetic strategy presented in this work. This provides a route to incorporating ferrocenyl moieties into polyphenylenes, by introducing the metal complex at an early synthetic stage. Despite the need for it to survive the reaction conditions of all subsequent steps, we felt confident that the good chemical stability and attractive materials properties of ferrocene offered a reasonable chance of success.

Interest in the fluxional processes of sterically demanding chiral propeller compounds of the type C_nAr_n has given rise to the limited examples of monoferrocenyl polyphenylene compounds in the literature to date, e.g., sterically crowded C_6Ph_5Fc (2), shown in Scheme 1.¹⁹ It is, however, important to expand the nature and type of such systems and to include electrochemical and spectroscopic evaluations of the resulting molecules, as illustrated by the work of Rathcore et al. in their investigations of hexakis(4-ferrocenylphenyl)benzene.²⁰

Results and Discussion

In general, the new ferrocenyl compounds synthesized in this work are yellow/red, crystalline, air-stable solids, soluble in common chlorinated and aromatic solvents, but mostly insoluble in hexane. The orange to red color is a result of an absorption band at around 440 nm and is characteristic of ferrocene compounds. All the complexes were studied spectroscopically and characterized by ¹H and ¹³C NMR and IR spectroscopy and accurate mass and ESI-mass spectrometry.

Compounds 1, 2, and 5 were synthesized by the [2+4]-cycloaddition reaction of ethynylferrocene,²¹ phenylethynylferrocene,²² and 1,4-bis(ferrocenyl)butadiyne,²⁴ respectively, with commercially available tetraphenylcyclopentadienone (tetracyclone) in a benzophenone melt at 200 °C. After work-up, column chromatography isolated polyphenylene 1 as an air-stable, orange-red, crystalline solid in 70% yield. 2 was isolated in a similar manner as an orange-yellow, air-stable solid in 36% yield. The NMR and IR spectroscopic data as well as mass spectrometry of 2 concurred with those already reported.¹⁹

Polyphenylenes **3** and **4** were synthesized by the Diels– Alder reaction of 1,1'-bis(phenylethynyl)ferrocene with 1.2 and 2.2 equiv of tetracyclone, respectively. 1,1'-Bis(phenylethynyl)ferrocene was synthesized by the Stille coupling of 1,1'-iodoferrocene with 2 equiv of phenylethynyltrimethylstannane.²³ Compound **3** was isolated as the mono-Diels– Alder adduct, whereas **4** was isolated as the diadduct. Compounds **3** and **4** were isolated as orange, crystalline solids in 44% and 18% yield, respectively. Compound **5** was isolated as a red, air-stable solid in 75% yield.

The novel polyphenylenes **3**, **4**, and **5** were fully characterized by NMR and IR spectroscopy as well as mass spectrometry.

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Full details of the characterization of all the compounds can be seen in the Experimental Section.

Cyclodehydrogenation. Given our interest in synthesizing ferrocenyl-supported PAHs, the cyclodehydrogenation of polyphenylenes 1, 2, 3, 4, and 5 was attempted; however only 1 underwent successful cyclodehydrogenation using AlCl₃ and CuCl₂. The cyclodehydrogenation of 1 yielded 6 (Scheme 1) in 15% yield as a pale yellow solid. As a step toward an organometallic model of an intercalated graphitic sheet, 6 was expected to possess interesting geometric and electronic properties.

Under the conditions for cyclodehydrogenation 1 also produced insoluble and intractable material. This accounts for the low yield of 6 and is believed to be a consequence of the partial oxidative decomposition of the ferrocene nuclei by Cu^{II} salts.¹⁵ Evidence for the successful cyclodehydrogenation came from the large aromatic shifts in the ¹H NMR spectrum of 6 on comparison with those of the ferrocenyl polyphenylene 1. The aromatic proton signals in the δ 6.6– 7.2 range, for 1, moved downfield to δ 7.2–9.8 in 6, as a direct result of the increase in ring-current-induced deshielding by the PAH.

Attempts to cyclodehydrogenate ferrocenyl polyphenylenes 2, 3, 4, and 5 to form the planar, ring-closed system were unsuccessful, yielding only black, insoluble, and uncharacterizable solids, indicating the complete decomposition of the polyphenylenes.

Single-Crystal X-ray Analysis. Room-temperature, singlecrystal X-ray diffraction of **1** was carried out to determine the solid-state molecular arrangement. Orange crystals of **1** were obtained, in air, from the slow diffusion of hexane into a dichloromethane solution of **1**.

All investigated crystals of **1** proved to be heavily twinned. The sample finally chosen consisted of at least five domains, four of which could be investigated. The structure was solved and refined for two domains, with an R_1 of 4.79%. It crystallized in space group $P\overline{1}$, and its molecular structure is shown in Figure 1. The propeller-like molecular structure shows twisting of the phenyl and ferrocene subunits with respect to the central phenyl ring, moving clockwise around the central ring, and starting at C1 the twist of the ferrocene moiety is 36° out of the plane formed by the central ring. The other phenyls rings are tilted by 56°, 58°, 70°, and 72°, respectively.

This is unusual but similar to the structure reported¹⁹ for **2**, where each peripheral ring is displaced slightly more than its preceding neighbor (from 51° for ferrocenyl ring to 120°). More common is the regular propeller configuration of C_6Ph_6 -type molecules with uniform twists on the order of 67° between the outer and central phenyl rings.²⁵

Molecules of 1 are offset stacked and head-to-tail to avoid steric interactions between the ferrocenyl units of neighboring molecules. The ferrocene moiety remains unperturbed by the presence of the polyphenylene, and the cyclopentadienyl rings of the ferrocene are 3° off planarity.

UV–Vis Absorption Spectroscopy. The electronic absorption spectra of ferrocene and its substituted derivatives have revealed that the metal-centered d_{z^2} orbital is generally the HOMO, and the combination of the d_{xz} and d_{yz} is the LUMO.^{13,26} The absorption around 440 nm in ferrocene is



Figure 1. The X-ray crystal structures of ferrocenyl polyphenylene 1.

Table 1. UV-Vis Data for Ferrocene and 1, 2, 3, 4, 5, and 6 in Toluene

compound	$\begin{array}{c} \lambda_{\rm max}, {\rm nm} \\ (\varepsilon, L {\rm mol}^{-1} {\rm cm}^{-1} \times 10^3) \end{array}$	low-energy d-d transition
Fc	327.0 (0.5)	438.5 (0.5)
1	344.0 (2.0)	447.5 (0.5)
2	350.5 (2.5)	464.5 (0.5)
3	358.0 (3.1)	460.0 (0.7)
4	300.0 (19.6), 359 (sh) (3.7)	464.0 (1.0)
5	324.0 (11.0), 359.0 (sh) (3.5)	453.0 (1.0)
6	302.5 (10.0), 312.0 (14.0), 355.0 (4.0), 371.5 (4.0), 405.0 (0.5)	ca. 440

thus assigned as the ${}^{1}E_{1g} \leftarrow {}^{1}A_{1g}$ ligand field (LF) transition ("d-d" transition) and the higher energy band around 325 nm as the ${}^{1}E_{2g} \leftarrow {}^{1}A_{1g}$ LF transition. Organometallics are highly covalent, so these metal-centered d orbitals actually have considerable ligand character and are sensitive to ligand binding.²⁷ Substitution onto a cyclopentadienyl ring particularly by conjugated acceptor groups is generally followed by drastic changes in the UV-vis absorption spectra.

The electronic absorption spectra of 1, 2, 3, 4, 5, and 6 were recorded in toluene, and the data are presented in Table 1. Excluding 6, each of the complexes displays two or three prominent absorption bands in the 300–600 nm region. Similar to other ferrocenyl species, they exhibit a weak low-energy band attributable to the d-d transition arising from the ferrocene moiety.^{27,28} These broad, low-energy features account for the orange to red colors of these compounds. The two weak absorption bands of the ferrocene unit ($\lambda = 327.0$ and 438.5 nm) are magnified, in some instances, indicating perturbation of the ferrocene frontier orbitals upon substitution.

In ferrocene there is a very weak feature at around 438.5 nm. The ferrocene derivatives in this study also display this typical ferrocenyl transition in the visible region; however they are shifted to the 440 to 465 nm region, again

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Figure 2. UV-vis absorption spectrum of 6 in toluene.

suggesting frontier orbital interaction between donor and acceptor.

In the UV-vis spectrum of 1 there is a peak at 344 nm and an additional broad feature at 447.5 nm. There are similar features in the spectrum of 2 at 350.5 and 464.5 nm and in the spectrum of 3 at 358 and 460 nm. The spectrum of 4 has a shoulder at 359 nm, a broad absorption at 464.0 nm, and an additional shoulder at 300 nm. This is mirrored in the spectrum of 5, which also has a shoulder at 359.0 nm, a broad absorption at 453 nm, and an additional band at 324 nm. 1, 2, 3, 4, and 5 show similar electronic properties but smaller HOMO-LUMO energy gaps than ferrocene, as reflected in the lower energy of their transitions.

An interesting question concerns how the electronic properties of the ferrocencyl moiety in 1 are effected by ring closure of the polyphenylene. The UV-vis spectrum of ferrocenyl PAH derivative **6** is very different from polyphenylene **1**, with four intense features in the 300-425 nm region (Figure 2). In the UV-vis spectrum of **6**, the broad signature of the ferrocene d-d transition almost disappeared, and instead only a small shoulder at around 440 nm occurs. It is likely that the weaker ferrocenyl band is hidden beneath the broad 405 nm band, which is assigned to a $\pi \rightarrow \pi^*$ transition. In addition, **6** is highly absorbing between 300 and 450 nm. In general, the spectrum of **6** is dominated by $\pi \rightarrow \pi^*$ absorption bands with high absorption coefficients (Table 1) and is reminiscent of spectra obtained for tribenzoperylene.

Due to insolubility, the UV-vis spectra for PAHs are often restricted to measurement in thin films (solid-state characterization), unless they are substituted by large solubilizing chains.²⁹ In Table 2 the ground-state absorption properties of **6** are compared to those of dodecyl-substituted tribenzoperylene.

Compound **6** can be considered to be an L-shaped molecule in which a ferrocene donor group is linked to a planar polyaromatic moiety. It is well known that the solubility of the simple PAH (tribenzoperylene, $C_{30}H_{16}$) fragment attached to the ferrocene unit in **6** is extremely low. It is necessary, in order to obtain soluble analogues of this PAH, to attach long solubilizing chains on the periphery.²⁹ The fact that its ferrocenyl analogue **6** is soluble in organic solvents suggests there is an underlying factor preventing



Table 2. UV–Vis Data of 6 and Dodecyl-Substituted Tribenzopervlene²⁹

Themesperytene						
compound	λ_{\max} (nm)					
5 ^a	312	355	372	405		
ribenzoperylene ^b	315	365	384	418		
^{<i>a</i>} Toluene. ^{<i>b</i>} Chlorof	orm.					
		C ₁₂ H ₂₅	C ₁₂ H ₂₅			



tribenzoperylene

Figure 3. Structures of ferrocenyl PAH 6 and tribenzoperylene.

aggregation. Aggregation of the PAH unit is caused by a $\pi-\pi$ stacking, which, in **6**, could be prohibited by the bulky ferrocenyl group. There appears to be little perturbation of the PAH fluorophore in **6**. The $\pi \rightarrow \pi^*$ transitions in the UV-vis spectra of the alkyl-substituted PAH are at the same energy as for the soluble ferrocene analogue. It is suggested, therefore, that steric interactions between individual ferrocenyl molecules impact on the ability of the PAH subunit to stack or form dimers. This has been seen in single-crystal X-ray studies of ferrocenyl molecules on the periphery of a columnar network.

Comparison of the spectral properties of **6** to tribenzoperylene serves as further evidence for the success of the cyclodehydrogenation reaction in forming the closed ring system of **6**. It shows that the $\pi \rightarrow \pi^*$ transitions of the PAH unit dominate the absorption spectrum of **6**. The UV-vis spectra of **6** and long chain substituted tribenzoperylene show extremely similar shape and λ_{max} values. Both spectra show three types (groups) of bands (α, β, p), which are typical of aromatic hydrocarbons. The β -bands appear around 315 nm, and the *p*-bands around 370 nm. The α -band at 410 nm is an extremely low intensity absorption band.

Investigations into the oxidation of substituted ferrocenes with air in acidic solutions have been carried out by numerous workers.³¹ It has been reported that the rate of the oxidation is influenced by the ability of a proton to coordinate to the iron atom. A greater reactivity can be accounted for by a specific, tilted conformation of the two cyclopentadienyl rings.³¹ The same authors also report a correlation between the wavelength of the low-energy band at around 450 nm (see Table 1), which is found to be sensitive to the inclination of the cyclopentadienyl rings of ferrocene,³¹ and the rate of oxidation in acidic solution. As an example, [2]ferrocenophane, which possesses tilted cyclopentadienyl rings, exhibits a longer wavelength absorption and facile protonation of its iron center.³¹

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 Table 3. Electrochemical Data for Ferrocenyl Complexes 1, 2, 3,

 4. 5. and 6^a

complex	$E^{\circ}(\mathbf{V})$	$\Delta E_{\rm p}~({\rm mV})$	
1	-0.05	117	
2	-0.08	81	
3	+0.03	90	
4	-0.16	79	
5	-0.06, 0.15	76, 76	
6	+0.04	70	

^{*a*} Redox potentials are given in dichloromethane and referenced vs the ferrocenium/ferrocene couple using platinum disk working electrode, Pt wire auxiliary electrode, Ag/Ag^+ reference electrode, 100 mV s^{-1} scan rate, with 0.1 M (Bu₄N)PF₆ as supporting electrolyte. ΔE_p is given by $E_{pa} - E_{pc}$.

The low-energy band (Table 1) of 1 appears at the shortest wavelength of the polyphenylenes synthesized and is the closest to that of ferrocene. In polyphenylenes 2, 3, 4, and 5 the low-energy bands are shifted to longer wavelengths than ferrocene by between 14.5 and 25.5 nm. Therefore the basicity of the iron center(s) in 2, 3, 4, and 5 would be expected to be high because of the increased nonplanarity of the cyclopentadienyl rings. The resulting accelerated protonation of the metal centers may have serious implications in the highly acidic conditions of oxidative cyclodehydrogenation and perhaps explains the failure of 2, 3, 4, and 5 to generate superaromatics.

Electrochemistry. Ferrocene/ferrocenium itself represents a strictly reversible one-electron redox couple, although in some derivatives reversibility may be significantly lowered by decomposition of the electrogenerated ferrocenium species.¹² Ferrocene substituents may also be regarded as a redox-active probe on a molecular level, since following the ferrocene/ferrocenium redox potentials offers a unique opportunity to detect alterations in the electronic structure of the ferrocene-derived molecules, as well as the metal– π -ligand bonding. It also provides information about the changes of electron density distribution and HOMO energies in a series of related compounds.¹²

Table 3 compares the redox potentials of, 1, 2, 3, 4, and 5, in dichloromethane (0.1 M (Bu_4N)PF₆ as electrolyte). Under the experimental conditions, all derivatives studied, except diferrocenyl 5, exhibit a fully reversible one-electron oxidation attributable to the ferrocene/ferrocenium couple. Derivative 5 displays two such reversible one-electron oxidations.

All potentials are quoted versus the $[Fc/Fc^+]$ couple, which had a potential of 0.51 V using the Ag/AgCl nonaqueous reference electrode used in this work. Peak separations are in the range $\Delta E = 70-120$ mV, close to the reversible limit. These values are similar to those of the ferrocene standard (160 mV under the same voltammetric conditions), indicating that the one-electron $[Fc/Fc^+]$ oxidation processes are electrochemically reversible in dichloromethane.

For **6** a reversible one-electron redox process was observed at $E^{\circ} = 0.04$ V with $\Delta E = 70$ mV, while the diferrocenyl, complex **5**, exhibits two redox processes at $E^{\circ} = -0.06$ and 0.15 V. The peak separations ($\Delta E = 76$ mV) and almost identical peak currents indicate two reversible one-electron oxidations occurring independently at each ferrocene center.

Although all the ferrocenyl compounds show reversible one-electron oxidation, it is interesting to note that the redox potentials of the ferrocene units show a broad range of values from -0.08 to 0.15 V, caused by the electronic effect of the substituents. The net result of the two synergic interactions between the metal and the ligand frontier orbitals and the E° of the resulting $[Fc/Fc^+]$ couple is dependent on the substitution of the ligand.^{10,32}

Compared to the ferrocene standard, the oxidation potentials of the ferrocenyl units in 1, 2, and 4 exhibit a slight cathodic (less positive) shift (50-160 mV). The relatively low value for the ferrocene oxidation potential indicates that these ferrocenyl species are electron rich. The ease of oxidation in the three related compounds could be attributed to the electron-donating ability of the polyphenylene core, stabilizing the oxidized form with respect to ferrocene itself.

The two redox potentials in diferrocenyl 5 could be assigned to the oxidation of the Fe(II)–Fe(II) complex to the mixed-valence Fe(II)–Fe(III) complex and, at a more positive potential, oxidation to the Fe(III)–Fe(III) complex. The first ($E^{\circ} = -0.06$ V), which is essentially the same as 1 ($E^{\circ} = -0.05$), is assigned to the Fc(polyphenylene) group and the second ($E^{\circ} = 0.15$ V) to oxidation of the ethynylferrocene substituent (ethynylferrocene: $E^{\circ} = 0.13$ V).

The redox potential of **3** is anodically shifted (30 mV) compared to ferrocene and is in between that of ferrocenyl polyphenylenes **1**, **2**, **4**, and **6**. Clearly the slight electronwithdrawing ability of the ethynylbenzene is being seen.

The cyclic voltammogram of **6** exhibits a redox potential of $E^{\circ} = 0.04$ V. The significant anodic shift (90 mV) as compared to the oxidation potential for **1** ($E^{\circ} = -0.05$ V) is due to the electron-withdrawing effect of the fully cyclized PAH substituent, which is bound directly to the ferrocenyl moiety. This makes oxidation of the ferrocene unit in **6** electrochemically more difficult than that of uncyclized **1** and ferrocene. A similar though lesser effect is seen for **3**, which shows a slight anodic shift (by 30 mV) compared to that of ferrocene. In this case it is due to the electron-withdrawing effect of the acetylene group.

Conclusions

Four novel ferrocenyl polyphenylenes, **1**, **3**, **4**, and **5**, have been synthesized and spectroscopically characterized. The redox chemistry of these ferrocenyl derivatives has been investigated by cyclic voltammetry and compared to ferrocene and the previously reported **2**. The molecular structure of **1** has been elucidated by single-crystal X-ray analysis.

The work describes the successful cyclodehydrogenation of 1 to the novel ferrocenyl PAH derivative 6 and demonstrates for the first time the conditions for the generation of metallo-organic superaromatics.

The electronic spectra of the complexes were measured in toluene. Polyphenylenes 1, 2, 3, 4, and 5 all display similar features in their UV-vis absorption spectra; however the spectral data support the proposition that the two cyclopentadienyl rings are significantly tilted in 2, 3, 4, and 5. Consequently, protonation of the iron atom of the ferrocene units in these compounds is expected to be accelerated, and their oxidation reactivity increased in acidic media during cyclodehydrogenation. Conversely the cyclopentadienyl rings in 1 are less tilted, and as a result, the ferrocenyl moiety was able to withstand cyclodehydrogenation to yield 6. The absorption spectrum of ferrocenyl complex 6 was dominated by the $\pi \rightarrow \pi^*$ absorption bands of the polycyclic aromatic substituent, and the absorption due to the d-d transitions at lower energy was effectively swamped. The electrochemistry

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of all the compounds was investigated by cyclic voltammetry in dichloromethane, and all derivatives exhibit the oneelectron reversible oxidation wave associated with the ferrocene/ferrocenium couple. The corresponding E° values are influenced by the electronic effects of the substituent and were found to support the aromatic shifts observed in the NMR data. The value of the oxidation potential of ferrocenyl 6 is considerably more positive than that of 1, due to the electron-withdrawing effect of the polyaromatic function directly attached to the ferrocene unit. The diferrocenyl polyphenylene derivative 5 displayed separated, reversible, one-electron-oxidation steps ($E^{\circ} = -0.06$ and 0.15 V), occurring independently at each ferrocenyl center. Oxidation of 5 thus involves two consecutive one-electron steps to give the corresponding mono- and then diferrocenium species in the potential region examined.

This work demonstrates the formation of an organometallic molecular graphene, which could have wide-reaching applications for the future study and production of molecular materials.

Experimental Section

Materials and Methods. Unless otherwise stated, all reactions were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Flash chromatography was performed using silica gel (Fluka 60) or activated alumina (Brockman I, Aldrich Chemical) as the stationary phase, and all separations were carried out in air. Tetraphenylcyclopentadienone (Aldrich) and ferrocene (Aldrich) were used as received. Ethynylferrocene,²¹ phenylethynylferrocene,²² 1,1'-bis(phenylethynyl)ferrocene,²³ and 1,4-bis(ferrocenyl)butadiyne²⁴ were synthesized according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded in CDCl₃ with (i) a Bruker Avance DPX-400 MHz spectrometer at the frequencies 400.13 MHz for ¹H and 100.6 MHz for ¹³C or (iii) an AV-600 MHz spectrometer at 600.13 MHz for ¹H and 150.6 MHz for ¹³C. The signals for ¹H and ¹³C spectra were referenced to TMS at δ 0.00, and coupling constants were recorded in hertz (Hz). Electrospray mass spectra were recorded on a micromass LCT tof electrospray mass spectrometer. Despite multiple attempts, it was not possible to obtain consistent, accurate elemental analysis results except for 1. This is not uncommon where large polyphenylene or thermally robust polyaromatic frameworks are involved. In the alternative the ¹H NMR spectra are provided for all other novel, numbered compounds (3-6) in the Supporting Information, and accurate mass spectra recorded against lucine enkephalin $(555.6 \text{ g mol}^{-1})$ are reported with accuracy within 5 ppm in all cases

Cyclic voltammetry was performed using a CH Instruments electrochemical analyzer model 600B and a conventional threeelectrode cell with a Ag/AgCl (saturated KCl) reference electrode. All solutions were degassed with N₂ before measurements were taken, and a blanket of N₂ was maintained over the solution for the duration of the experiment. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte for all the experiments.

All photophysical studies were carried out with solutions contained within $1 \times 1 \text{ cm}^2$ quartz cells in HPLC grade solvents and were degassed using N₂ bubbling. UV-visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer and the data analyzed using UVProbe software.

X-ray analysis was performed with a Bruker SMART APEX CCD diffractometer using graphite-monochromised Mo K α ($\lambda = 0.71073$ Å) radiation at 153 K. A full sphere of data was obtained using the omega scan method. The data reduction was

performed using SMART and SAINT-NT (v. 6.2). Intensities were corrected for Lorentz and polarization effects and for absorption using SADABS (v. 2).³³ Space groups were determined from systematic absences and checked for higher symmetry. The structures were solved by direct methods using SHELXS (v. 5.1) and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL (v. 5.1).³⁴ The functions minimized were $w(F_o^2 - F_c^2)$, with $w = [s^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$. In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions.

General Procedure for the Synthesis of 1, 2, 3, 4, and 5 via [2+4]-Cycloaddition Diels-Alder Reaction. A mixture of appropriate acetylene (1 equiv), tetraphenylcyclopentadienone (1 equiv, or 1.2 or 2.2 equiv in the case of 3 and 4), and benzophenone was mixed in a round-bottomed flask and attached to an air condenser. The mixture was heated at 200 °C for 48 h. The reaction mixture was subsequently cooled to RT, and the residue was extracted into dichloromethane and filtered. After removal of the solvent the recovered material was subjected to flash chromatography (SiO₂, 1:1 hexane/dichloromethane).

Compound 1. Yield: 70%, mp 213 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (s, 1H, Ph H), 7.17–6.66 (m, 20H, Ph H), 4.06 (s, 5H, Cp H), 3.96 (t, 2H, J = 2 Hz, Cp H), 3.89 (t, 2H, J = 2 Hz, Cp H). ¹³C NMR (100 MHz, CDCl₃): δ 141.2, 140.3, 139.7, 139.4, 139.2, 139.1, 137.0, 136.9, 136.0, 130.7, 130.5, 130.4, 130.2, 128.9, 126.7, 126.1, 125.8, 125.5, 125.2, 124.8, 124.4, 124.2, 85.7, 69.4, 68.5, 66.7. Anal. Calcd for C₄₀H₃₀Fe: C, 84.80; H, 5.33. Found: C, 84.68; H, 5.38. ESI-MS (CH₃CN): m/z (%) [M]⁺ 566.3 (100) (calcd 566.4). IR (KBr disk, cm⁻¹): ν (C–H st) 3080, 3055, 3022, ν (C=C st) 1599, 1494, 1441, 696.

Compound 2. Yield: 36%, mp > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.08 (m 10H, Ph H), 6.81 (m, 15H, Ph H), 3.88 (s, 2H, Cp H), 3.80 (s, 2H, Cp H), 3.73 (s, 5H, Cp H). ¹³C NMR (100 MHz, CDCl₃): δ 131.7, 130.8, 130.6, 126.2, 125.8, 125.3, 124.6, 124.5, 72.8, 68.9, 66.5. ESI-MS (CH₃CN): m/z (%) [M]⁺ 642.6 (100) (calcd 642.6). ESI-MS (CH₃CN): calculated for C₄₆H₃₄Fe [M]⁺ m/z 642.2010, found 642.2036. IR (KBr disk, cm⁻¹): ν (C–H st) 3080, 3056, 3022, ν (C=C st) 1599, 1497, 1441, 699, ν (CH rock, Cp) 1108, 1070, 1029, 1006.

Compound 3. Yield: 44%, mp 239–240 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.49–7.43 (m, 2H, Ph H), 7.33–7.32 (m, 3H, Ph H), 7.16–7.06 (m, 10H, Ph H), 6.85–6.77 (m, 15H, Ph H), 4.08 (t, 2H, J = 2 Hz, Cp H), 3.94 (t, 2H, J = 2 Hz, Cp H), 3.81 (t, 2H, J = 2 Hz, Cp H), 3.63 (t, 2H, J = 2 Hz, Cp H). ¹³C NMR (150 MHz, CDCl₃): δ 141.67, 141.47, 141.39, 140.64, 140.46, 139.62, 136.73, 133.08, 131.94, 131.21, 131.07, 130.84, 128.11, 126.61, 126.35, 126.12, 126.09, 125.75, 124.81, 88.37, 87.79, 85.56, 84.20, 74.11, 71.98, 70.60, 69.92. ESI-MS (methanol) for C₅₄H₃₈Fe: [M]⁺ calculated *m*/*z* 742.2323, found *m*/*z* 742.2297. IR (KBr disk, cm⁻¹): ν (C–H st, aromatic) 3079, 3053, 3023, ν (C≡C st) 2207, ν (C≡C st): 1599, 1494, 1441, ν (C–H rock Fc) 1070, 1026, 1010.

Compound 4. Yield: 18%, mp > 200 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 7.00 (m, 20H, Ph H), 6.78 (m, 30H, Ph H), 3.43 (s, 4H, Cp H), 3.19 (s, 4H, Cp H). ESI-MS (toluene) for C₈₂H₅₈Fe: [M]⁺ calculated *m*/*z* 1098.3888, found *m*/*z* 1098.3873. IR (KBr disk, cm⁻¹): ν (C–H st, aromatic) 33078, 3053, 3022, ν (C=C st) 1599, 1464, ν (C–H rock Fc) 1073, 1027.

Compound 5. Yield: 75%, mp > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.29 (m, 5H, Ph H), 7.00 (m, 3H, Ph H), 6.84 (m, 10H, Ph H), 6.72 (m, 2H, Ph H), 4.40 (s, 2H, Cp H), 4.22 (s, 5H, Cp H), 4.20 (s, 4H, Cp H), 4.09 (s, 7H, Cp H). ¹³C NMR (100 MHz, CDCl₃): δ 144.5, 141.4, 141.3, 140.4, 140.2, 140.1, 139.8, 138.6, 136.9, 131.3, 130.8, 130.7, 130.4, 126.8, 126.6, 126.1, 126.0, 125.6, 125.1, 124.8, 124.7, 122.6, 100.8, 87.2, 84.6, 71.3, 70.2,

⁽³³⁾ SAINT+; Bruker-AXS, 1997-1999.

^{(34) (}a) Sheldrick, G. M. SADABS; University of Gottingen, 1998.
(b) Sheldrick, G. M. Acta Crystallogr. 1990, A46, 467. (c) Sheldrick, G. M. SHELX-97, University of Gottingen, 1997.

69.4, 68.3, 66.5, 65.9. ESI-MS (CH₃CN): m/z (%) [M]⁺ 774.2 (100) (calcd 774.5). ESI-MS (CH₃CN): calculated for C₅₂H₃₈Fe₂ [M]⁺ m/z 774.1672, found 774.1686. IR (KBr disk, cm⁻¹): ν (C-H st) 3082, 3056, 3022, ν (C=C st) 2211, ν (C=C st): 1600, 1496, 1441, 697, ν (CH rock, Cp) 1106, 1069, 1027, 1001.

Synthesis of 16-Ferrocenyl(tribenzo[*e*;*g*,*h*,*i*;*k*])perylene (6). Compound 1 (180 mg; 0.318 mmol), AlCl₃ (700 mg; 5.25 mmol), and CuCl₂ (700 mg; 5.21 mmol) were stirred in CS₂ (60 mL) at 25 °C for 48 h under an argon atmosphere. The black solid was allowed to settle and the CS₂ removed by cannula. The solid was dried *in vacuo* and stirred in dilute ammonia solution. The product was extracted into chloroform and dried over MgSO₄. Chromatography (SiO₂, 7:3 hexane/diethyl ether).

Yield: 15%, mp > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.83 (s, 1H, Ph H), 9.07 (d, 2H, ³J_{HH} = 8 Hz, Ph H), 9.01 (t, 2H, ³J_{HH} = 7 Hz, Ph H), 8.92 (d, 2H, ³J_{HH} = 8 Hz, Ph H), 8.71 (d, 1H, ³J_{HH} = 8 Hz, Ph H), 8.11 (m, 3H, Ph H), 7.89 (t, 1H, ³J_{HH} = 7 Hz, Ph H), 7.83 (t, 1H, ³J_{HH} = 7 Hz, Ph H), 7.59 (t, 1H, ³J_{HH} = 7.5 Hz, Ph H), 7.24 (t, 1H, ³J_{HH} = 7.5 Hz, Ph H), 4.77 (t, 2H, J = 2 Hz, Cp H), 4.50 (t, 2H, J = 2 Hz, Cp H), 4.12 (s, 5H, Cp H). ¹³C NMR (100 MHz, CDCl₃): δ 133.8, 130.7, 130.1, 130.0, 129.8, 129.7, 129.6, 129.5, 129.4, 127.5, 125.8, 124.7, 124.4, 124.3, 124.0, 130.2, 127.4, 127.1, 126.7, 126.4, 126.2, 126.0, 124.1, 123.4, 123.1, 122.9, 121.6, 121.4, 121.2, 120.8, 70.7, 69.5, 67.9. ESI-MS (toluene): m/z (%) [M]⁺ 559.8 (100) (calcd 560.4). ESI-MS (toluene): calculated for C₄₀H₂₄Fe [M]⁺ m/z 560.1227, found 560.1226. IR (KBr disk, cm⁻¹): ν (C–H st) 3083, 3071, ν (C=C st) 1459, 1383, 1261, ν (CH rock, Cp) 1096, 1075, 1021.

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Supporting Information Available: The crystallographic data for compound **1** as well the complete ¹H NMR spectra for novel compounds **3**, **4**, **5**, and **6**. Tables showing H–H TOCSY and HMQC information for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.