Syntheses and Properties of Multiferrocenylated Corannulenes

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The syntheses and properties of corannulenes bearing different numbers and types of ferrocenyl groups are described. Six different monoferrocenylated corannulenes were synthesized, and the crystal structure of 1-corannulenyl-1′-(ferrocenyl)benzene was elucidated by single-crystal X-ray analysis. Further, diferrocenylated corannulenes bearing methyl or trifluoromethyl groups are reported. Buckybowls with four

and five ferrocenyl substituents were synthesized from tetrabromocorannulene and the symmetrical pentachlorocorannulene. The molecular structure and nutshell-like crystal packing of a tetraferrocenylated corannulene was determined by single-crystal X-ray analysis. Additionally, all compounds presented herein were subjected to electrochemical and optical measurements in solution.

Introduction

Buckybowls are bowl-shaped subunits of fullerenes and have become available in applicable scale only over the past few years.[1] Unlike planar aromatic systems, these nonplanar hydrocarbons exhibit different properties on the inside and outside of their bowl-shaped surfaces.[2] The first buckybowl, corannulene ($C_{20}H_{10}$), was discovered in 1966 and is the smallest of its species.[3] Unlike polycyclic aromatic hydrocarbons (PAHs), it is not rigid but undergoes a rapid bowl-to-bowl inversion in solution.[4] Similar to fullerenes, a noteworthy property of corannulene is its electron-acceptor ability.[5] Corannulene can be chemically reduced up to the tetraanion by alkali metals, if the reduction is performed in dry aprotic solvents under inert conditions. Odd-numbered reduction states are paramagnetic species, and even-numbered states are diamagnetic.[6]

After the prediction of the solid-state structure of the tetraanion ($C_{20}H_{10}^{4-}$) as an octaanionic dimer in 1994,[6] the group of Petrukhina presented the first crystal structure of a corannulene tetraanion with lithium cations in 2012[7] and confirmed the predicted sandwichlike structure. In the solid state, the lithium cations are arranged between, above and below two drastically flattened corannulene tetraanions corresponding to a $[Li_5(C_{20}H_{10}^{4-})_2]^{3-}$ formula; further studies under modified conditions followed.[8]

Electrochemically, only reduction up to the trianion has been observed, and all three reductions show a reversible character in the presented setup.[9]

The coordination chemistry of corannulene is manifold;[10] interestingly, η^2-[11] and η^6-corannulene[12] compounds show metal coordination only at the convex face (outside of the bowl) of the molecule when a single metal atom is bound to corannulene.[13] The coordination of two ruthenium centres on opposite sides of corannulene completely flattens the formerly bowl-shaped molecule.[13,14] Furthermore, in a cyclopalladated corannulene, the coordination of the palladium atom to the corannulene rim, assisted by pyridine, drastically influenced the packing structure in the solid state and the aggregation behaviour in solution.[15] Other σ-bound platinum and nickel complexes were also prepared.[16]

On the other hand, ferrocene (Fc) has been known for over 60 years[17] and is not only used widely in catalysis[18] and pharmaceuticals[19] but also in redox systems. Starshaped oligoferrocenes are promising materials as multiredox systems and in molecular electronics. Ridgid starshaped perferrocenyl molecules with a benzene core were reported by Vollhardt et al.[20] and Astruc et al.[21] Hexaferrocenylbenzene, reported by Vollhardt, shows three separated redox processes, which suggests that there is electrochemical communication between the ferrocenyl substituents. On the other hand, the redox stars reported by Astruc have ferrocenyl substituents connected to the benzene core through ethynyl spacers and show no direct or only insignificant electronic interactions between the ferrocenyl substituents; however, they do show frustration effects and electrostatic interactions.[21]

The group of Lang studied five-membered heterocyclic aromatic systems with directly bonded ferrocenyl substitu-

ents such as multiferrocenyl pyrroles[22] and thiophenes.[23] The disubstituted 2,5-diferrocenyl-1-phenyl-1*H*-pyrrole exhibits the largest separation of oxidation potentials among ferrocenyl aromatics reported to date, as a result of the decreased energy gap between the ferrocenyl moieties and the heterocyclic core accompanied by an increased delocalization in the heterocyclic core. Spectroelectrochemical measurements of different diferrocenylthiophenes showed that they exhibit different degrees of interaction between the ferrocenyl moieties depending on their positions at the heteroaromatic thiophene core.[23b] 2,3,4,5-Tetraferrocenyl-thiophene showed separated redox waves but no intervalence charge transfer (IVCT) absorptions in the near-IR region when oxidized stepwise; thus, only electrostatic communication (with no electronic communication) of the ferrocenyl substituents was observed.[23a]
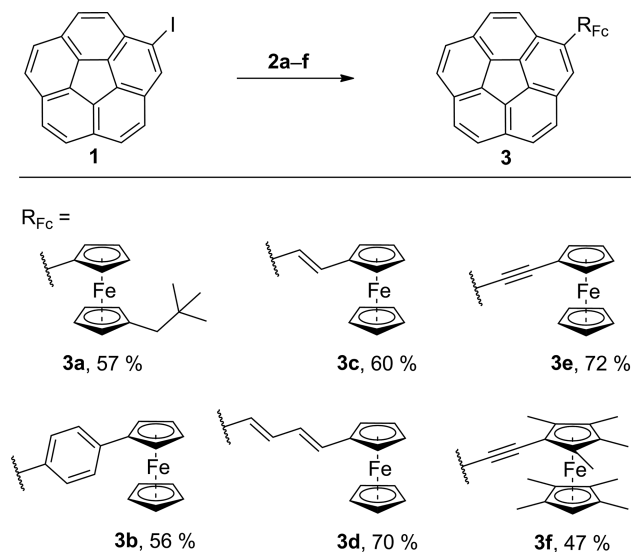
Recently, we presented corannulenyl-[24] and sumanenyl-ferrocenes,[25] synthesized by Negishi-type cross-coupling (NCC) conditions, and especially focussed on their unique solid-state structures. Herein, we present a comprehensive study of mono-, di-, tetra- and pentaferrocenyl-substituted corannulenes. The ferrocenyl substituents are connected directly and through spacers to the corannulene rim.

Results and Discussion

Syntheses

All compounds in this study were prepared from halogenated precursors by straightforward palladium- or nickel-catalyzed cross-coupling reactions.

For monosubstituted derivatives, iodocorannulene (**1**) proved to be a versatile precursor. A variety of cross-coupling reaction conditions were applied, as summarized in Scheme 1. Under NCC conditions similar to those previously reported for corannulenylferrocene, 1-corannulenyl-1′-neopentylferrocene (**3a**) and 1-corannulenyl-4-ferrocenyl-benzene (**3b**) could be obtained in satisfying yields. The corresponding zinc reagents are very sensitive species and were prepared in situ by lithium–halogen exchange at low temperatures in tetrahydrofuran (THF) followed by the addition of anhydrous zinc chloride. Compound **1**, palladium(II) acetate and triphenylphosphane were added as solids at ambient temperature to this solution. After the mixture was heated to reflux for the time given in Scheme 1, both products were isolated in ca. 60% yield. Purification by column chromatography with deactivated silica gel (1% triethylamine was added to solvents) was sufficient to obtain analytically pure compounds. Vinylferrocenyl and butadienylferrocenyl substituents were introduced under Heck conditions, which yielded products **3c** and **3d** in slightly higher yields after column chromatography. The Sonogashira-type reactions of ethynylferrocenes with **1** yielded ferrocenylethynylcorannulene (**3e**) and the corresponding octamethylethynylferrocene derivative (**3f**).
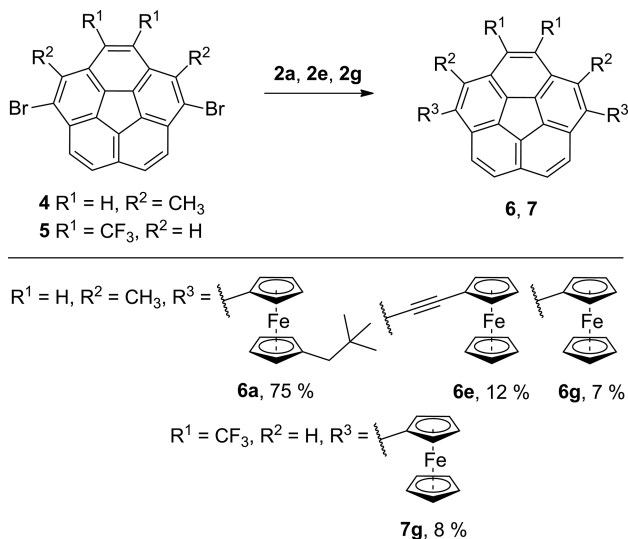

Scheme 1. Syntheses of monoferrocenylcorannulenes **3**. Compound **3a**: 1-neopentyl-1′-ferrocenylzinc chloride (**2a**, 1.6 equiv.), palladium acetate (3 mol-%), triphenylphosphane (6 mol-%), THF, 80 °C, 17 h (57%); **3b**: 4-ferrocenylphenylzinc chloride (**2b**, 2.0 equiv.), palladium acetate (1 mol-%), triphenylphosphane (2 mol-%), THF, 60 °C, 48 h (56%); **3c**: vinylferrocene (**2c**, 1.1 equiv.), potassium acetate (1.5 equiv.), tetra-*n*-butylammonium bromide (1.0 equiv.), palladium acetate (10 mol-%), DMF, 80 °C, 15 h (60%); **3d**: butadienylferrocene (**2d**, 1.1 equiv.), potassium acetate (2.5 equiv.), tetra-*n*-butylammonium bromide (1 equiv.), palladium acetate (5 mol-%), DMF, 80 °C, 24 h (70%); **3e**: ethynylferrocene (**2e**, 1.2 equiv.), potassium *tert*-butoxide (2.0 equiv.), tris-(dibenzylideneacetone)dipalladium(0) [Pd$_2$(dba)$_3$, 1 mol-%], THF, 80 °C, 4 h (72%); **3f**: 1-ethynyl-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**2f**, 2.0 equiv.), potassium *tert*-butoxide (3.5 equiv.), Pd$_2$(dba)$_3$ (3.5 mol-%), DMF, 80 °C, 5 h (47%).

The compounds are air-stable solids ranging from orange to red and purple. Compound **3a** is a deep red solid with a relatively low melting point of 61 °C, whereas **3b** is an orange solid with a strong tendency to crystallize. Monoferrocenylated corannulenes are C_1-symmetric and show complex ^{1}H NMR spectra consisting of a singlet and partially overlapping AB patterns for the corannulene rim protons and the typical resonances of mono- and 1,1′-substituted ferrocene moieties. The ^{13}C NMR spectra exhibit individual signals for each of the corannulene carbon atoms, which can be assigned to the hub, spoke and rim carbon nuclei as suggested by Scott et al.[26]

As dibromination of corannulene is not regioselective, diferrocenylated corannulenes were prepared from previously reported 1,6-dibromo-2,5-dimethylcorannulene (**4**)[27a] and 1,6-dibromo-3,4-bis(trifluoromethyl)corannulene (**5**, Scheme 2).[28]

NCC with ferrocenylzinc chloride (**2g**) gave 1,6-diferrocenyl-2,5-dimethylcorannulene (**6g**) in 7% yield. The low yield can be explained by the low solubility of the compound, which complicates the purification process by column chromatography and leads to only a small amount of analytically pure compound, although the crude yield was satisfying. The use of **2a** as reactant gave a satisfying yield of 75% of **6a** owing to the increased solubility and, hence,
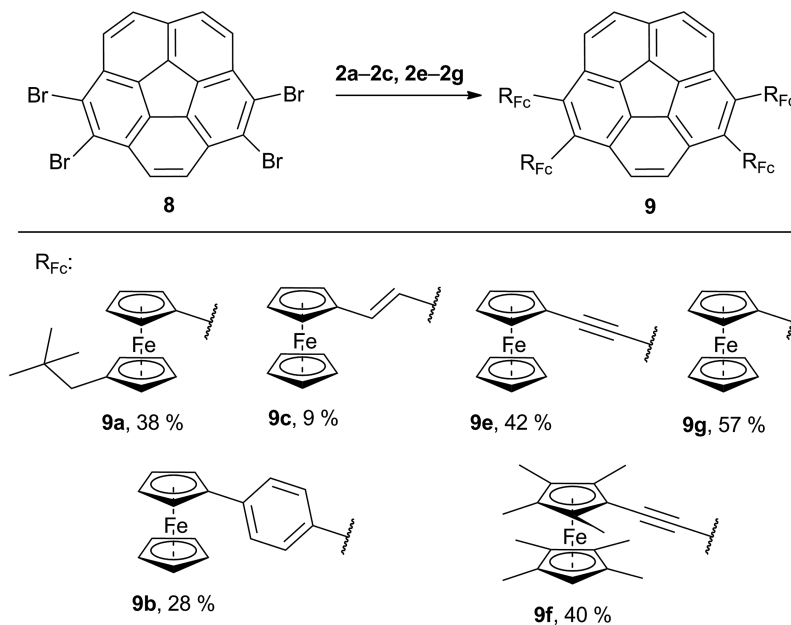
Scheme 2. Diferrocenylated corannulenes **6** and **7**. Compound **6a**: **2a** (4.0 equiv.), palladium(II) acetate (2 mol-%), triphenylphosphane (4 mol-%), THF, 65 °C, 19 h (75%); **6e**: **2e** (3.0 equiv.), palladium acetate (5 mol-%), triphenylphosphane (10 mol-%), copper iodide (11 mol-%), toluene/triethylamine (2:1), 70 °C, 24 h (12%); **6g**: **2g** (4.0 equiv.), palladium(II) acetate (4 mol-%), triphenylphosphane (8 mol-%), THF, 70 °C, 18 h (7%); **7g**: **2g** (9.0 equiv.), palladium(II) acetate (4 mol-%), triphenylphosphane (8 mol-%), THF, 60 °C, 24 h (8%).

easier purification. Compound **6e** could be prepared under Sonogashira-type conditions. All of these compounds possess C_s symmetry in solution. Thus, the ^{1}H NMR spectra show two sets of signals for the corannulene rim protons. One singlet for the two protons neighbouring the methyl groups and an AB-type set of signals for the other four protons can be observed. The methyl groups resonate at δ = 3.01 ppm.

Trifluoromethyl groups provide a strong –I effect, which facilitates the reduction of the corannulene moiety.[29] The crude product of **7g** contained a large amount of biferrocene, which possesses a very similar R_f value to that of **7g**. After a two-step column chromatography with different mixtures of n-pentane and dichloromethane (5:1 and 10:1), the pure product could be isolated in a moderate yield of 8%. The solubility of the wine-red **7g** is rather low in common organic solvents.
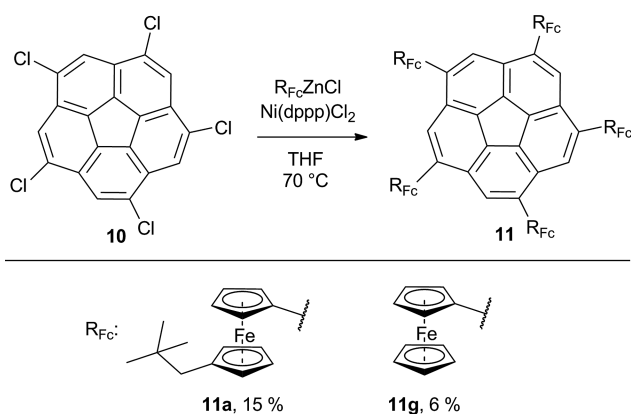
Although 1,2,5,6-tetrabromocorannulene (**8**)[27b] possesses very low solubility in common organic solvents, it is nevertheless a suitable reactant for a variety of cross-coupling reactions, which were pursued according to the procedures described for **3a**–**3f** with some minor adjustments (Scheme 3) to the reaction conditions for the brominated species. All of these compounds possess C_s symmetry in solution; thus, the ^{1}H and ^{13}C NMR spectra resemble those of the previously mentioned compounds **6a**–**6g** and have similar sets of signals for the rim, spoke and hub atoms.

Scheme 3. Tetraferrocenylated corannulenes **9**. Compound **9a**: **2a** (8.0 equiv.), palladium(II) acetate (4 mol-%), triphenylphosphane (8 mol-%), THF, 62 °C, 48 h (38%); **9b**: **2b** (8.0 equiv.), palladium(II) acetate (4 mol-%), triphenylphosphane (8 mol-%), THF, 70 °C, 24 h (28%);%); **9c**: (1) **2c** (4.5 equiv.), potassium carbonate (45 equiv.), tetrabutylammonium bromide (18 equiv.) and palladium(II) acetate (10 mol-%), DMF, 80 °C, 48 h; (2) **2c** (4.5 equiv.), palladium(II) acetate (10 mol-%), 80 °C, 24 h (9%); **9e**: **2e** (4.4 equiv.), copper(I) iodide (20 mol-%), palladium(II) acetate (10 mol-%), triphenylphosphane (20 mol-%), toluene/triethylamine (2:1), 70 °C, 20 h (42%); **9f**: **2f** (4.4 equiv.), palladium(II) acetate (5 mol-%), triphenylphosphane (10 mol-%), copper(I) iodide (5 mol-%), diisopropylamine, 80 °C, 56 h (40%); **9g**: **2g** (8.0 equiv.), palladium acetate (4 mol-%), triphenylphosphane (8 mol-%), THF, 60 °C, 48 h (57%).

The overall yields are satisfying except for the low yield of **9c**, which can be explained by the very low solubility of the product. Surprisingly, it possesses the lowest solubility of all of the synthesized ferrocenylated corannulenes.

The symmetrical 1,3,5,7,9-pentachlorocorannulene (**10**) was first synthesized by the group of Scott and is a versatile building block for a variety of pentasubstituted corannulene derivatives.[30] The syntheses are straightforward by Ni-mediated cross-coupling between the chlorinated corannulene and the ferrocenylzinc chloride species (Scheme 4). The yields are again strongly dependant on the solubility of the intermediates and the product. The purification of pentaferrocenylated **11g** without the solubilizing alkyl chain was exceedingly difficult. First, residual ferrocene was removed by sonication of the crude material with hexane. After filtration through a plug of silica gel, a red solid was obtained. MALDI mass spectrometry identified the pentasubstituted derivative as the main product with hexa- and tetrasubstituted byproducts, which could be removed by careful preparative TLC (PTLC) on silica gel with pentane/dichloromethane (1:1) as eluent. However, the other fractions still contained small amounts of the product. The C_5 symmetry of **11a** and **11g** leads to straightforward NMR spectra. Only one singlet for the five chemically equivalent protons on the corannulene rim was observed in the ^{1}H NMR spectrum. Again, the ferrocenyl group shows the expected signals for mono- and 1,1′-substituted derivatives. The ^{13}C NMR spectra exhibit one signal each for the corannulene hub, spoke and rim atoms as well as the *ipso* carbon nuclei.

Scheme 4. Pentaferrocenylated corannulenes **11**. Compound **11a**; **2a** (10.0 equiv.), dichloro[1,3-bis(diphenylphosphino)propane]-nickel [Ni(dppp)Cl₂, 30 mol-%], THF, 60 °C, 3 d (15%); **11g**: **2g** (15.0 equiv.), Ni(dppp)Cl₂ (30 mol-%), THF, 67 °C, 29 h (6%).

Crystal Structures

Compound **3b** crystallizes in the monoclinic space group $P2_1$ with two molecules in the asymmetric unit. The bowl depths of the corannulene moieties of both molecules (0.832 and 0.895 Å) are within the average range for corannulene (0.87 Å)[26] and in accordance with the calculated bowl depth (see Supporting Information). Interestingly, although the ferrocenyl moiety of one molecule is in the *exo* position

relative to the corannulene bowl (see Figure 1), the other ferrocenyl moiety is in the *endo* position (not depicted). By introduction of the phenyl spacer, the energy difference between the *endo* and *exo* positions probably becomes negligible. The cyclopentadienyl (Cp) rings of both molecules are only 2.4 and 4.8° distorted from perfectly eclipsed conformations within the ferrocenyl unit.
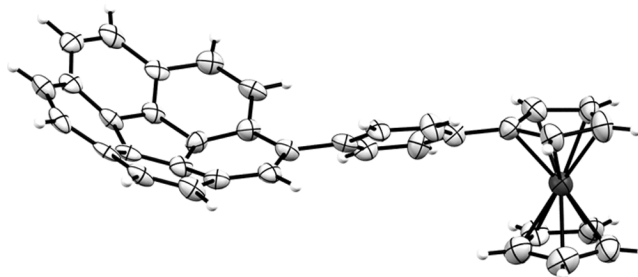

Figure 1. Mercury[31] representation rendered with POV-Ray[32] of a single molecule of **3b** determined by X-ray diffraction (carbon: light grey; iron: deep grey; hydrogen: white). Ellipsoids are drawn at 50% probability. Two molecules are present in the asymmetric unit, *exo*-**3b** and *endo*-**3b**; *exo*-**3b** is depicted and possesses a bowl depth of 0.8322(1) Å [0.8951(1) Å for *endo*-**3b**].

The torsion angle between the phenyl and cyclopentadienyl rings differs for both molecules. In one molecule, both are nearly perfectly in plane (deviation 2.31°), and in the other molecule of the asymmetric unit, the torsion angle amounts to 29.15° (32.33° calculated). In both molecules, the phenyl spacer is not in the plane with the connected six-membered ring of the corannulene moiety (31.71 and 35.93°; 42.80° calculated); therefore, an extended conjugated π-system from the corannulene moiety to the ferrocenyl unit does not occur.

The molecular packing of corannulenes can be greatly influenced by ferrocene substitution, for example, as previously shown in corannulenylferrocene and 1,1′-dicorannulenylferrocene.[24] The structure is dominated by CH···π interactions,[33] but it also shows a remotely columnar arrangement with slipped stacking along the crystallographic *b* axis. There are π···π interactions with alternating distances of 3.41 and 3.88 Å within one strand of bowls (centroid-to-centroid distances of two six-membered rings). The strands of molecules interact through CH···π contacts. The closest CH···π interactions are 2.81 Å between a proton of the phenyl spacer and an unsubstituted cyclopentadienyl ring of a neighbouring molecule and 2.98 Å between a rim proton of the corannulene moiety and an unsubstituted cyclopentadienyl ring of a ferrocenyl substituent of an adjacent molecule (Figure 2).

Compound **9b** crystallizes in the triclinic space group $P\bar{1}$ from a toluene solution layered with isopropyl alcohol. Two molecules of **9b** and three toluene solvent molecules form the asymmetric unit. The bowl depths are slightly shallower than that of corannulene (0.837 and 0.793 Å; 0.820 Å calculated), as a result of the steric strain caused by the phenyl groups.[34] All ferrocenyl substituents are in *exo* positions to the corannulene bowl (Figure 3). On both molecules, the cyclopentadienyl rings are nearly in a plane with the phenyl
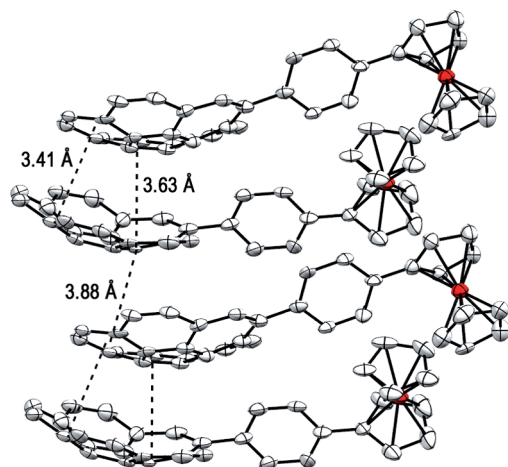
Figure 2. Packing structure of **3b** in Mercury[31] representation rendered with POV-Ray.[32]

spacer but not in a plane with the attached six-membered rings of the corannulene moieties. Once again, no considerable delocalization of the π system can be assumed.
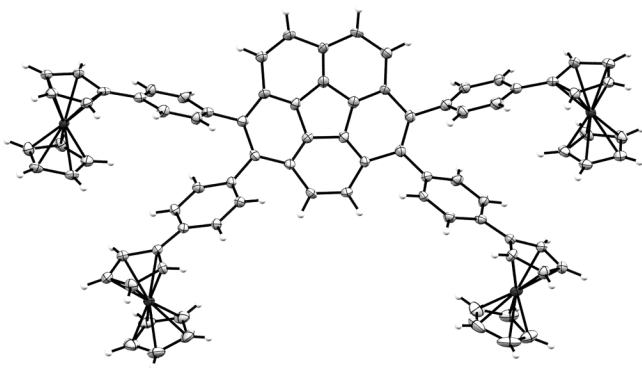

Figure 3. Single molecule of **9b** in Mercury representation,[31] rendered with POV-Ray[32] as determined by X-ray diffraction. Ellipsoids are drawn at 50% probability. Two molecules of **9b** and three additional toluene solvent molecules are present in the asymmetric unit. The bowl depths of the two **9b** molecules are 0.7931(1) and 0.8373(1) Å.

Two molecules of **9b** surround one toluene molecule in a nutshell-like arrangement. The toluene molecule within the cavity is located 4.04 and 3.80 Å from a six-membered ring of the corannulene moiety (Figure 4). Two additional toluene molecules are present on the outside of this arrangement and are within ca. 3.20 Å of the corannulene rim, located on the same side of one molecular sandwich.

The overall packing motif does not show a columnar array. The nutshell motif repeats in a slightly shifted packing along the crystallographic *a* axis. This arrangement is supported by C–H···π contacts of the ferrocenyl groups between the nutshell and CH···π interactions between the phenyl spacer and the outer corannulene bowl of an adjacent dimer. The rim protons of the corannulene bowl also show C–H···π contacts to the centre of the phenyl spacer
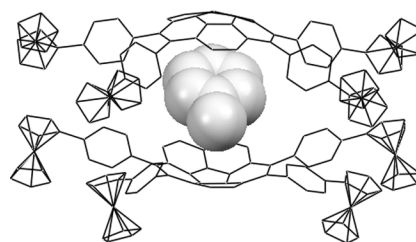

Figure 4. Mercury representation[31] rendered with POV-Ray[32] of the nutshell-like arrangement of two molecules of **9b** surrounding one toluene molecule (space-filling model). The two outer toluene molecules and protons are omitted for clarity.

(3.04 Å). Along the crystallographic *b* axis, the main contact is the CH···π interaction of an outer toluene molecule with the next dimer (3.12 Å) along this axis. Along the crystallographic *c* axis, only an interaction of one ferrocenyl substituent with an adjacent nutshell-like formation can be observed. The CH···π contact between the two unsubstituted cyclopentadienyl rings is 3.13 Å. The X-ray crystallographic data for 3b and 9b are summarized in Table 1.

Table 1. X-ray crystallographic details of **3b** and **9b**.

	3b	9b
Formula	$C_{36}H_{22}Fe$	$(C_{84}H_{58}Fe_4)$ $_2(C_7H_8)_3$
Mass	510.39	2857.89
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P1$
a [Å]	17.617(3)	12.706(3)
b [Å]	7.6767(12)	13.142(3)
c [Å]	17.983(2)	23.320(6)
α [Å]	90	77.024(6)
β [Å]	103.483(13)	77.709(6)
γ [Å]	90	64.576(6)
V [Å³]	2365.1(6)	3397.0(16)
T [K]	110(2)	120(2)
Z	4	1
Total reflections	12217	65932
Unique reflections	5198	32554
R_{int}	0.1552	0.0459
Final R_1 values [$I > 2\sigma(I)$]	0.0811	0.0568
Final $wR_2(F^2)$ values (all data)	0.2012	0.1453
GOF on F^2	1.035	1.073

UV/Vis Spectroscopy

All of the ferrocenylcorannulenes are strongly coloured, from purple to orange depending on the spacer and the ferrocenyl moiety attached. To quantify these colour differences and, thus, the different optical properties of the corannulenes, UV/Vis spectroscopy measurements were conducted. Although ferrocene is strongly coloured in the solid state, it does not show strong absorbance.[35] Thus, the UV/Vis maxima mainly arise from the corannulene core itself or from intramolecular charge transfer (ICT) between the corannulene core and the attached ferrocenyl moieties.

All of the monosubstituted compounds show strong absorption maxima between λ = 430 and 230 nm that also tail

into the visible region of the spectra (for spectra and tables, see Supporting Information). The main absorption maxima of corannulenylferrocene (λ = 294 and 250 nm) and **3a** (λ = 293 and 251 nm), both of which tail into the visible region, confirm the negligible influence of the neopentyl group on the electronic structure of the molecule. The shapes of both spectra are similar to the spectrum of corannulene, though the maxima at higher wavelength experience a bathochromic shift, whereas the maxima at lower wavelength stay nearly identical. For the different spacers, the bathochromic shift increases in the order none < phenyl = ethynyl < vinyl < butadienyl. The larger redshift of butadienyl-bridged **3d** can be explained by the extended π system and the good delocalization, as exemplarily shown by the highest occupied molecular orbital [HOMO, see the Supporting Information for the HOMOs and lowest unoccupied molecular orbitals (LUMOs) of selected compounds]. In comparison, the absolute sizes of the other ferrocenylcorannulenes are smaller; thus, they possess smaller π systems. Phenyl-bridged **3b** is of similar size but possesses a less-favourable molecular geometry (compare the solid-state structures). Wu et al. examined multiethynyl corannulenes empirically and found that a higher substituent count leads to longer emission wavelengths.[27a] Diederich et al. reported that the exact positioning of the substituents in their push–pull corannulenes and, hence, the molecular symmetry influences the electronic structure of the compound.[36] The soluble neopentylferrocenyl substituent allowed the preparation of singly, doubly, quadruply and quintuply ferrocenylated soluble corannulenes for direct comparison (Figure 5). The effect of the amount of substituents on the electronic properties could be examined, whereas the effect of different substitution patterns could not be elucidated owing to synthetic limitations.
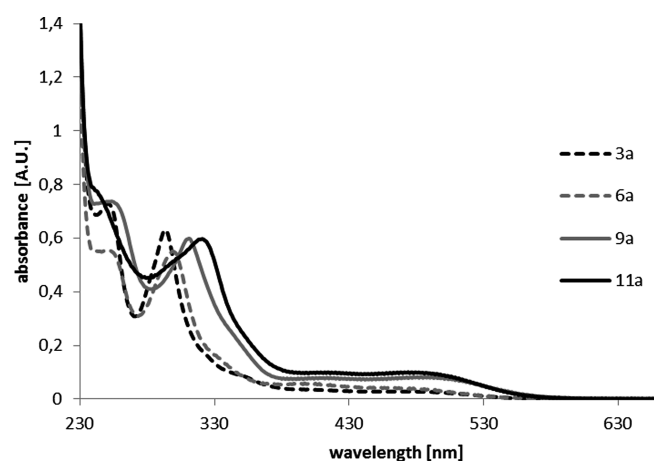

Figure 5. UV/Vis spectra of once (**3a**), twice (**6a**), four times (**9a**) and five times neopentylferrocenyl–substituted (**11a**) corannulenes; 1×10^{-5} M in dichloromethane.

A general trend can be observed: an increasing degree of ferrocenylation results in a bathochromic shift of the absorption maximum centred at λ = 300 nm ($\pi \rightarrow \pi^*$). The broad absorption maxima at λ = 380–550 nm could be assigned to a charge transfer that consequently increases and shows a stronger redshift with an increasing number of ferrocenyl substituents.

Electrochemistry

Cyclic voltammetry and square-wave voltammetry measurements were conducted in a Schlenk cell with three platinum wires as electrodes. Decamethylferrocene (ferrocene for **3f** and **9f**) was used as an internal standard. All redox values were calculated against the ferrocene/ferrocenium redox couple. Dry THF was used as the solvent as it is capable of stabilizing the reduced species. The dry and stabilizing conditions are very important, because corannulene-based anions are very sensitive towards moisture. The frontier orbitals of representative compounds of each class were calculated and are visualized in the Supporting Information. In general, the basic calculations show that the frontier orbitals have similar electronic structures and symmetry as those reported for the comprehensively studied multiethynylcorannulenes.[27a] Monoferrocenylated class **3** compounds have their HOMOs localized on the respective ferrocenyl substituents, which suggests that the oxidation of the ferrocenyl substituent and reduction of the corannulene bowl should be facile. Diferrocenylated classes **6** and **7** possess significant delocalization of the HOMO on both ferrocenyl substituents; thus, two oxidation waves should be observable. Tetraferrocenylated compounds **9** follow this trend and give reason to expect oxidation waves for each ferrocenyl substituent, whereas the HOMO of pentaferrocenylated **11g** is located only on four of the five ferrocenyl substituents, probably for symmetry reasons.

The monoferrocenylated species showed reversible oxidation waves for the ferrocenyl unit in the anodic region and quasireversible to irreversible reductions at the corannulene units in the cathodic region. The redox potentials of the ferrocenyl units are within the range of ferrocene itself.[24] Thus, no relevant electronic interactions between the substituents and the corannulene moiety are expected to be present. The oxidations of the vinyl- and butadienyl-bridged compounds **3c** and **3d**, as well as that of **3a**, are shifted to slightly more negative potentials. The same can be observed for **3f**, but the shift in this case might arise from the eight methyl groups at the ferrocenyl subunit, which facilitate the oxidation by their +I effect. The reduction potentials of the corannulene moieties are similar within the group of the monoferrocenylated compounds and only slightly higher than the potential of unsubstituted corannulene (–2.47 V). Monosubstituted corannulenes show one or two reduction processes, sometimes followed by chemical processes (see Supporting Information). For the reduction process, **3f** shows the least-negative potential (–2.30 V) and **3a** shows the lowest potential (–2.48 V). For **3d**, two well-separated reduction waves can be observed.

Diferrocenylated compounds **6a** and **6e** show one reversible oxidation process when the common conducting salt

NBu$_4$PF$_6$ or highly non-coordinating conducting salts such as tetra-*n*-butylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [BArF$_{(CF_3)}$] or tetra-*n*-butylammonium tetrakis(pentafluorophenyl)borate [BArF$_{(C_6F_5)}$] are employed.[37] The reduction of the corannulene is clearly irreversible for both compounds, possibly because of the +I effect of the additional methyl groups at the corannulene bowl. The two ferrocenyl units are not expected to interact either electrostatically or electronically, as no splitting of the redox wave was observed when BArF$_{(CF_3)}$ was used for the additional electrochemical measurements. On the other hand, the electron-withdrawing trifluoromethyl groups of **7g** facilitate the reduction process on the corannulene unit, and two reductions could be observed. As a result, **7g** shows a very small HOMO–LUMO gap of 1.89 V.

The tetraferrocenylated compounds are particularly interesting in their electrochemical behaviour with two groups of ferrocenyl substituents in close proximity. If the ferrocenyl substituents are connected through spacers, only one oxidation process occurs in THF/NBu$_4$PF$_6$. However, if the ferrocenyl unit is directly attached to the corannulene rim, two slightly separated processes were observed; these processes correspond to two two-electron oxidations originating from the two groups of chemically different ferrocenyl substituents. BArF$_{(CF_3)}$ was employed as a weakly coordinating conducting salt for the latter compound, and the redox processes of **9a** split into four well-separated processes, as depicted in Figure 6. The two groups of ferrocenyl substituents each show additional splitting, which results in four addressable one-electron oxidations.

In the cyclic voltammograms of the ethynyl-bridged compounds **9e** and **9f**, a split into two oxidation steps was observed, whereas the phenyl-bridged species still showed only one oxidation process. Not more than one reduction of the corannulene core was observed for all tetraferrocenylated compounds.

The pentaneopentyl compound **11a** showed one oxidation process with NBu$_4$PF$_6$ as a conducting salt, almost identical to that of the ferrocenyl, and no statement about
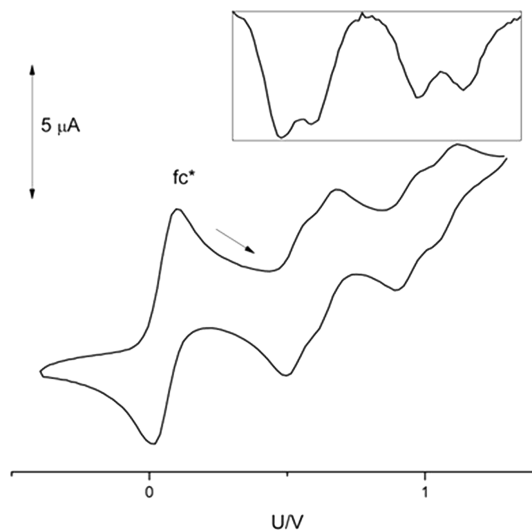

Figure 6. CV and SW (inlet) measurements of **9a** in dichloromethane with BArF$_{(CF_3)}$ (0.1 M) as a conducting salt at a scan rate of 100 mV.

the amount of electrons could be made. Measurements with BArF$_{(CF_3)}$ showed five separated one-electron processes with $\Delta E \approx 0.1$ V. Although the difference in voltage between these five redox processes is not very large, at least three of them show a reversible character. This demonstrates that the pentacation and all of the oxidized intermediates of the symmetrically ferrocenylated **11a** can be generated (Figure 7) to provide access to a large highly ferrocenylated π surface with precisely addressable oxidations states.

If only the use of weakly coordinating anions separates the oxidation processes of multiply ferrocenylated corannulenes, no electronic communication between the ferrocenyl units can be expected. Thus, instead electrostatic effects that arise from the close proximity of the ferrocenyl substituents are assumed to be the cause of these separated redox processes.[21] The electrochemical data of the studied compounds are summarized in Table 2.

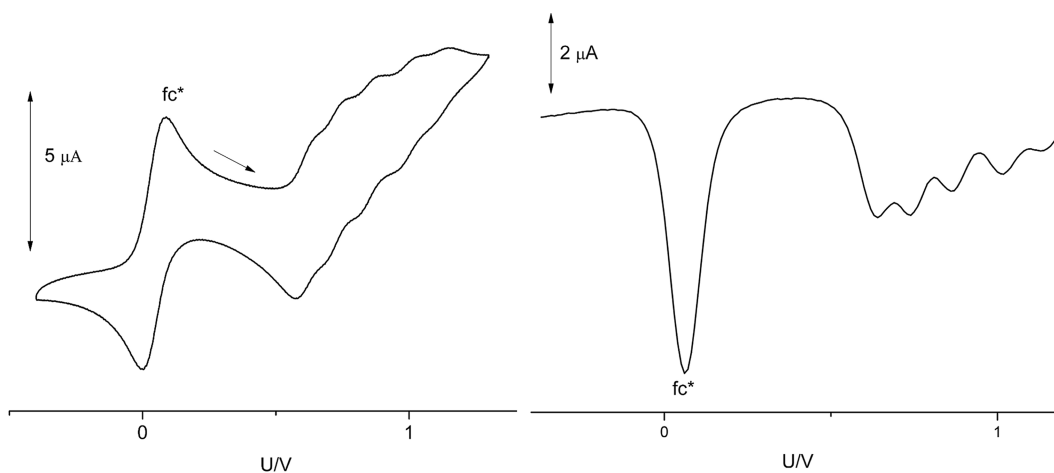

Figure 7. Left: Cyclic voltammogram of **11a**. Right: SW voltammogram of **11a**. Both recorded in dichloromethane with BArF$_{(CF_3)}$ (0.1 M) as conducting salt. Decamethylferrocene (fc*) was added as an internal standard, scan rate 100 mV/s.

Table 2. Electrochemical data of studied compounds.[a]

	E^0 Oxidation [V]	E^0 Reduction [V]	Electrochemical HOMO–LUMO gap [eV]
Corannulenylferrocene[24]	0.02	–2.51, –2.99$_{irrev}$	2.53
3a	–0.01	–2.48	2.47
3b	0.03	–2.43	2.46
3c	–0.02	–2.36$_{irrev}$	2.34
3d	–0.03	–2.28, –2.53	2.26
3e	0.13	–2.33$_{qrev}$	2.46
3f	–0.25*	–2.30*	2.05
6a	–0.03	–2.48$_{irrev}$	2.45
	–0.02[b]		
6e	0.10	–2.25$_{irrev}$	2.35
7g	0.07[c]	–1,82$_{irrev}$, –2.15$_{irrev}$[c]	1.89
	0.08[d]	–1.89$_{qrev}$, –2.17[d]	
9a	0.06, –0.07	–2.48	2.41
	0.42, 0.28, –0.03, –0.14[b]		
9b	–0.02	–2.33$_{qrev}$	2.31
9c	–0.03	–2.27$_{irrev}$	2.24
9e	0.10	–1.98	2.08
	0.61, 0.15[b]		
9f	–0.24*	–2.07	1.83
	–0.18, –0.36[b]		
9g	0.09, –0.03	–2.45	2.42
11a	–0.01	–2.40	2.39
	0.47, 0.36, 0.20, 0.07, –0.02[b]		

[a] Measurements were conducted in THF with 0.1 M tetrabutylammonium hexafluorophosphate. E^0 values were taken from square-wave measurements if possible. In cyclic voltammetry measurements, $E^0 = (E_{ox} + E_{red})/2$ was calculated. Electrochemical HOMO–LUMO gaps are determined as $E(HOMO) = e[E_{ox}^{onset}] + 4.8$; $E(LUMO) = e[E_{red}^{onset}] + 4.8$; $E_{Gap} = E(HOMO) - E(LUMO)$. qrev: quasireversible process, irrev: irreversible process, * measured with ferrocene as internal standard. Further information and voltammograms are provided in the Supporting Information. [b] Measurement conducted in dichloromethane with 0.1 M BArF$_{(CF_3)}$. [c] Measurement conducted in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate. [d] Measurement conducted in dichloromethane with 0.1 M BArF$_{(C_6F_5)}$.

Conclusions

Unprecedented multiferrocenylated corannulenes bearing, one, two, four and five ferrocenyl groups at the rim of the bowl-shaped polycyclic aromatic hydrocarbon were synthesized from known halogenated corannulenes. Several compounds were structurally elucidated by single-crystal X-ray analyses, and their structural properties were discussed and compared to computational data and the structures of known buckybowls. Their optical and electrochemical properties were elucidated and they showed distinct properties depending on the spacer attached as well as the symmetry and number of ferrocenyl substituents attached. If weakly coordinating anions are employed for electrochemical measurements, the soluble tetra- and pentaferrocenylated corannulenes allowed the specific oxidation of up to four and five attached ferrocenyl moieties, respectively. This gives access to manifold tailor-made multiredox systems, which can be controlled by the choice of spacer and soluble ferrocenyl groups, and their HOMO–LUMO gaps cover a wide range.

Experimental Section

Techniques: All experiments were performed under standard Schlenk conditions under an argon atmosphere or in an argon-filled MBraun glovebox (model LAB master SP).

Chemicals: Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl before use and further purified by trap-to-trap distillation for electrochemical use. Dichloromethane was dried with activated alumina by using an MBraun solvent system (model MB SPS-800) or distilled from calcium hydride and further purified by trap-to-trap distillation for electrochemical use. Triethylamine and diisopropylamine were distilled from calcium hydride; N,N-dimethylformamide (DMF) was distilled from phosphorus pentoxide. Corannulene (IUPAC name dibenzo[ghi,mno]fluoranthene) was synthesized according to the previously published methods.[38] Butadienylferrocene (**2d**),[39] 1-ethynyl-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**2f**),[40] 1-bromo-1′-neopentylferrocene,[41] 1-iodo-4-ferrocenylbenzene,[42] iodocorannulene (iododibenzo[ghi,mno]-fluoranthene, **1**),[24] 1,2,5,6-tetrabromocorannulene (1,2,5,6-tetrabromodibenzo[ghi,mno]fluoranthene, **8**),[38] 1,6-dibromo-2,5-dimethylcorannulene (1,6-dibromo-2,5-dimethyldibenzo[ghi,mno]-fluoranthene, **4**),[27a] 1,3,5,7,9-pentachlorocorannulene (1,3,5,7,9-pentachlorodibenzo[ghi,mno]fluoranthene, **10**),[43] BArF$_{(CF_3)}$[37] and BArF$_{(C_6F_5)}$[44] were synthesized according to reported methods.

Instrumentation: Melting points were determined with a Gallenkamp melting point apparatus. IR spectra were recorded with a Nicolet 5 SXC FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector [signals are denoted as follows: s (strong), m (medium) and w (weak)]. ^1H, ^{19}F and ^{13}C NMR spectra were measured with a JEOL ECS 400 spectrometer or with a Bruker AVIII 700 spectrometer at 23 °C. CDCl$_3$ and CD$_2$Cl$_2$ were used as solvents, if not stated otherwise, and the residual solvent peak was taken as an internal standard (^1H NMR: CDCl$_3$ δ = 7.26 ppm, CD$_2$Cl$_2$ δ = 5.30 ppm; ^{13}C NMR: CDCl$_3$ δ = 77.0 ppm, CD$_2$Cl$_2$ δ = 54.0 ppm; always proton-decoupled). Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS); ^{19}F NMR spectra were referenced to external CFCl$_3$. Mass spectra were measured with a MAT CH7A instrument (EI, 80 eV, 3 kV) at the given temperature for each sample (high-resolution masses were

determined by the peak-match method against perfluorokerosene) or with a Bruker Ultrafex II TOF/TOF V instrument. ESI-TOF spectra were measured with an Agilent 6210 ESI-TOF instrument. UV/Vis spectra were measured with a Perkin–Elmer Lambda 9 UV/Vis/NIR spectrometer and Hellma Analytics 111-QS cuvettes. Dichloromethane was used as solvent, and a compound concentration of 1×10^{-5} M was used. Cyclic voltammetry measurements were performed with a MaterialsM 510 (20V/1A) potentiostat, an ALS/CH Instruments electrochemical analyzer model 620c or a VersaSTAT 3 Princeton Applied Research potentiostat with a Schlenk measuring cell with three platinum wires as electrodes. A conducting salt concentration of 0.1 M was used. Linear scan voltammetry and chronoamperometric measurements as well as differential pulse voltammetry measurements were performed with a VersaSTAT 4 Princeton Applied Research potentiostat with a classic carbon or micro-platinum working electrode (WE), a platinum counter electrode (CE) and a silver pseudoreference electrode (RE). TLC (precoated) analysis and PTLC (precoated) was performed with Merck Silica gel 60 F_{254}.

Single-crystal X-ray structure determination was performed with a Bruker-AXS SMART 1000 diffractometer fitted with a CCD; the data set of **5** was collected with a Bruker Kappa ApexII duo diffractometer. Data collection, reduction and empirical absorption correction were performed by using the SMART, SAINT and SADABS programs, respectively;[45] the SHELX program package[46] was used for structure solution and refinement.

1-Corannulenyl-1′-neopentylferrocene (3a): 1-Bromo-1′-neopentylferrocene (83 mg, 0.25 mmol, 1.6 equiv.) was dissolved in THF (2 mL) and cooled to –30 °C. *n*-Butyllithium (0.11 mL, 2.5 M in *n*-hexane, 1.8 equiv.) was added dropwise. After the mixture was stirred for 30 min at –30 °C, anhydrous zinc(II) chloride (100 mg, 0.74 mmol, 3 equiv.) was added in one batch, and stirring at –30 °C was continued for 30 min. The reaction mixture was warmed to room temp. and stirred for a further 30 min. Iodocorannulene (**1**, 56 mg, 0.15 mmol, 1 equiv.), palladium(II) acetate (3 mol-%) and triphenylphosphane (6 mol-%) were added in one batch and the red reaction mixture was stirred at 80 °C for 17 h. The solvent was removed, and the residue was purified by silica gel column chromatography with *n*-pentane/dichloromethane (40:1) including 1% triethylamine. The product was obtained as a deep red solid (44 mg, 57%) from the fourth fraction, m.p. 61 °C. ^{1}H NMR (700 MHz, CD$_2$Cl$_2$): δ = 8.15 (AB, ^{3}J = 8.8 Hz, 2 H, H$_{rim}$), 8.06 (s, 1 H, H$_{rim}$), 7.88–7.81 (m, 6 H, H$_{rim}$), 4.89 (s, 2 H, H$_{Cp}$), 4.42 (s, 2 H, H$_{Cp}$), 4.07 (s, 2 H, H$_{Cp}$), 4.06 (s, 2 H, H$_{Cp}$), 2.22 (s, 2 H, CH$_2$), 0.74 (s, 9 H, CH$_3$) ppm. ^{13}C NMR (175 MHz, CD$_2$Cl$_2$): δ = 140.07 (1 C, C$_{ipso}$), 136.48 (1 C, C$_{hub}$), 136.41 (1 C, C$_{hub}$), 136.14 (1 C, C$_{hub}$), 136.02 (1 C, C$_{hub}$), 134.92 (1 C, C$_{hub}$), 131.55 (1 C, C$_{spoke}$), 131.48 (1 C, C$_{spoke}$), 131.12 (1 C, C$_{spoke}$), 130.95 (1 C, C$_{spoke}$), 130.39 (1 C, C$_{spoke}$), 128.15 (1 C, CH$_{rim}$), 127.83 (1 C, CH$_{rim}$), 127.74 (1 C, CH$_{rim}$), 127.65 (1 C, CH$_{rim}$), 127.41 (1 C, CH$_{rim}$), 127.32 (1 C, CH$_{rim}$), 127.25 (1 C, CH$_{rim}$), 127.22 (1 C, CH$_{rim}$), 124.85 (1 C, CH$_{rim}$), 87.82 (1 C, C$_{Cp}$), 85.30 (1 C, C$_{Cp}$), 72.50 (2 C, C$_{Cp}$), 70.93 (2 C, C$_{Cp}$), 70.47 (2 C, C$_{Cp}$), 70.34 (2 C, C$_{Cp}$), 45.01 (1 C, CH$_2$), 32.06 [1 C, C(CH$_3$)$_3$], 29.59 (3 C, CH$_3$) ppm. FTIR: $\tilde{\nu}$ = 3081 (w, br.), 3027 (w, br.), 2946 (m, sh), 2946 (m, sh), 2861 (m, sh), 1896 (w, br.), 1617 (w, br.), 1474 (m, sh), 1463 (m, sh), 1433 (w, sh), 1407 (w, sh), 1390 (m, sh), 1361 (m, sh), 1229 (m, sh), 1199 (w, sh), 1132 (w, sh), 1084 (w, sh), 1042 (m, sh), 1025 (m, sh), 953 (w, sh), 907 (m, sh), 872 (m, sh), 825 (s, sh), 749 (s, sh), 698 (m, sh), 666 (m, sh), 655 (m, sh), 643 (m, sh), 613 (w, sh), 583 (m, sh), 563 (m, sh), 541 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^{+}$ 504.1540; found 540.1570.

1-Corannulenyl-4-ferrocenylbenzene (3b): 1-Iodo-4-ferrocenylbenzene (163 mg 0.42 mmol, 2 equiv.) was dissolved in THF (2 mL) and cooled to –20 °C. *n*-Butyllithium (0.2 mL, 2.5 M in *n*-hexane, 2.4 equiv.) was added dropwise, and the reaction mixture was stirred at –20 °C for 30 min. Anhydrous zinc(II) chloride (100 mg, 0.73 mmol, 3.5 equiv.) was added in one batch, and stirring at –20 °C was continued for 30 min. After the mixture was stirred at room temp. for 30 min, palladium(II) acetate (1 mol-%), triphenylphosphane (2 mol-%) and iodocorannulene (**1**, 80 mg, 0.21 mmol, 1 equiv.) were added, and the orange reaction mixture was stirred at 60 °C for 48 h. Water (20 mL) and dichloromethane (20 mL) were added. The organic layer was separated, washed with water (4× 30 mL) and dried with sodium sulfate. Silica gel column chromatography with *n*-pentane/dichloromethane (4:1) as solvent yielded **3b** (61 mg, 56%) as an orange solid. Crystals were grown by evaporation of a dichloromethane/ethanol solution, m.p. 223 °C (dec.). ^{1}H NMR (700 MHz, CDCl$_3$): δ = 7.95 (s, 1 H, H$_{rim}$), 7.92 (d, ^{3}J = 8.8 Hz, 1 H), 7.90–7.81 (m, 7 H), 7.76 (d, ^{3}J = 7.8 Hz, 2 H), 7.69 (d, ^{3}J = 7.8 Hz, 2 H), 4.78 (s, 2 H), 4.42 (s, 2 H), 4.17 (s, 5 H) ppm. ^{13}C NMR (176 MHz, CDCl$_3$): δ = 141.74 (1 C, C$_{ipso}$ Ph-cor), 139.06 (1 C, C$_{ipso}$ Ph-Fc), 137.26 (1 C, C$_{ipso}$ cor-Ph), 136.42 (1 C, C$_{hub}$), 136.24 (1 C, C$_{hub}$), 135.90 (1 C, C$_{hub}$), 135.49 (1 C, C$_{hub}$), 135.28 (1 C, C$_{hub}$), 131.00 (1 C, C$_{spoke}$), 130.95 (1 C, C$_{spoke}$), 130.90 (1 C, C$_{spoke}$), 130.71 (1 C, C$_{spoke}$), 130.01 (1 C, C$_{Ph}$), 129.75 (1 C, CH$_{rim}$), 127.39 (1 C, CH$_{rim}$), 127.39 (1 C, CH$_{rim}$), 127.27 (1 C, CH$_{rim}$), 127.13 (1 C, CH$_{rim}$), 127.04 (1 C, CH$_{rim}$), 126.97 (1 C, CH$_{rim}$), 126.95 (1 C, CH$_{rim}$), 126.49 (s, C$_{ph}$), 125.41 (1 C, CH$_{rim}$), 85.00 (s, C$_{Cp-ipso}$), 69.74 (1 C, C$_{Cp}$), 69.16 (1 C, C$_{Cp}$), 66.68 (s, C$_{Cp}$) ppm. FTIR: $\tilde{\nu}$ = 3027 (w, sh), 2923 (w, sh), 1607 (w, sh), 1526 (w, sh), 1409 (m, sh), 1312 (m, sh), 1260 (m, sh), 1103 (m, sh), 1084 (m, sh), 1018 (m, sh), 1000 (m, sh), 888 (m, sh), 826 (s, sh), 807 (m, sh), 693 (m, sh), 663 (m, sh), 624 (m, sh), 572 (m, sh), 546 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^{+}$ 510.1071; found 510.1071.

(E)-1-(2-Ferrocenyl)ethenylcorannulene (3c): Iodocorannulene (**1**, 92 mg, 0.24 mmol, 1 equiv.), vinylferrocene (**2c**, 34 mg, 0.26 mmol, 1.1 equiv.), palladium(II) acetate (10 mol-%), potassium acetate (36 mg, 0.37 mmol, 1.5 equiv.) and tetra-*n*-butylammonium bromide (47 mg, 0.24 mmol, 1 equiv.) were dissolved in anhydrous DMF (2.8 mL). After the reaction mixture was degassed three times, it was heated for 15 h at 80 °C. After the mixture cooled to room temp., dichloromethane (20 mL) was added, and the dark red solution was washed with water (3× 100 mL). After the solution was dried with sodium sulfate and filtered, evaporation of the solvent and silica gel PTLC with *n*-pentane/dichloromethane (3:1) afforded **3c** (40 mg, 60%) as a red solid from the third fraction, m.p. 200 °C. ^{1}H NMR (700 MHz, CD$_2$Cl$_2$): δ = 8.04 (AB, ^{3}J = 8.8 Hz, 2 H, H$_{rim}$), 7.88–7.81 (m, 7 H, H$_{rim}$), 7.39–7.32 (AB, ^{3}J = 16 Hz, 2 H, H$_{vinyl}$), 4.63 (s, 2 H, H$_{Cp-sub}$), 4.39 (s, 2 H, H$_{Cp-sub}$), 4.23 (s, 5 H, H$_{Cp}$) ppm. ^{13}C NMR (175 MHz, CD$_2$Cl$_2$): δ = 138.90 (1 C, C$_{ipso}$), 136.71 (1 C, C$_{hub}$), 136.56 (1 C, C$_{hub}$), 136.21 (1 C, C$_{hub}$), 136.13 (1 C, C$_{hub}$), 132.45 (1 C, CH$_{vinyl}$), 131.93 (1 C, C$_{spoke}$), 131.68 (1 C, C$_{spoke}$), 131.40 (1 C, C$_{spoke}$), 131.21 (1 C, C$_{spoke}$), 129.63 (1 C, C$_{spoke}$), 127.94 (1 C, CH$_{rim}$), 127.85 (1 C, CH$_{rim}$), 127.72 (1 C, CH$_{rim}$), 127.59 (1 C, CH$_{rim}$), 127.44 (1 C, CH$_{rim}$), 127.34 (1 C, CH$_{rim}$), 126.36 (1 C, CH$_{rim}$), 124.06 (1 C, CH$_{rim}$), 123.42 (1 C, CH$_{rim}$), 83.99 (1 C, C$_{Cp-ipso}$), 70.08 (2 C, C$_{Cp}$), 69.95 (5 C, C$_{Cp}$), 67.79 (2 C, C$_{Cp}$) ppm. FTIR: $\tilde{\nu}$ = 3085 (w, br.), 3030 (m, sh), 2847 (m, sh), 1891 (w, sh), 1723 (m, sh), 1610 (m, sh), 1459 (m, sh), 1409 (m, sh), 1310 (m, sh), 1267 (m, sh), 1246 (m, sh), 1778 (m, sh), 1135 (m, sh), 1043 (m, sh), 1027 (m, sh), 995 (m, sh), 812 (s, sh), 742 (s, sh), 682 (m, sh), 557 (m, sh) cm^{-1}. EI-MS (170 °C): *m/z* (%) = 460.0894 (100) [M]$^{+\cdot}$ (calcd. 460.0914), 337 (71), 395 (15) [M – C$_5$H$_5$]$^{+\cdot}$, 121 (10) [CpFe]$^{+}$, 56 (4) Fe^{+}.

1-[(1*E*,3*E*)-4-(Ferrocenyl)buta-1,3-dienyl]corannulene (3d): Iodocorannulene (**1**, 67 mg, 0.18 mmol, 1 equiv.), butadienylferrocene (**2d**, 47 mg, 0.20 mmol, 1.1 equiv.), potassium acetate (44 mg, 0.45 mmol, 2.5 equiv.), tetra-*n*-butylammonium bromide (57 mg, 0.18 mmol, 1 equiv.) and palladium(II) acetate (5 mol-%) were dissolved in DMF (3 mL). After the dark red solution was degassed three times, it was stirred at 80 °C for 24 h. After the solution cooled to room temp., dichloromethane (10 mL) was added, and the organic layer was washed with water (3× 10 mL), dried with sodium sulfate and filtered. Evaporation of the solvent, followed by silica gel column chromatography with *n*-pentane/ethyl acetate (20:1) afforded a red solid. Purification by preparative TLC on alumina (type T) with *n*-pentane/toluene (1:1) yielded **3d** (53 mg, 70%) from the third fraction, m.p. 208 °C. ^{1}H NMR (700 MHz, CD$_2$Cl$_2$): δ = 7.99 (AB, ^3J = 8.7 Hz, 2 H, H$_{rim}$), 7.85–7.77 (m, 7 H, H$_{rim}$), 7.29–7.16 (m, 2 H, H$_{butadienyl}$), 6.73–6.59 (m, 2 H, H$_{butadienyl}$), 4.51 (s, 2 H, H$_{Cp-sub}$), 4.36 (s, 2 H, H$_{Cp-sub}$), 4.20 (s, 5 H, H$_{cp}$) ppm. ^{13}C NMR (175 MHz, CD$_2$Cl$_2$): δ = 138.07 (1 C, C$_{ipso}$), 136.42 (1 C, C$_{hub}$), 136.15 (1 C, C$_{hub}$), 135.87 (1 C, C$_{hub}$), 135.76 (1 C, C$_{hub}$), 135.74 (1 C, C$_{hub}$), 133.74 (1 C, CH$_{butadiene}$), 132.94 (1 C, CH$_{butadiene}$), 131.24 (1 C, C$_{spoke}$), 131.12 (1 C, C$_{spoke}$), 130.88 (1 C, C$_{spoke}$), 130.75 (1 C, C$_{spoke}$), 129.18 (1 C, C$_{spoke}$), 127.89 (1 C, CH$_{rim}$), 127.89 (1 C, CH$_{rim}$), 127.64 (1 C, CH$_{rim}$), 127.49 (1 C, CH$_{rim}$), 127.48 (1 C, CH$_{rim}$), 127.40 (1 C, CH$_{rim}$), 127.40 (1 C, CH$_{rim}$), 127.25 (1 C, CH$_{rim}$), 127.16 (1 C, CH$_{rim}$), 127.01 (1 C, CH$_{rim}$), 126.89 (1 C, CH$_{rim}$), 125.81 (1 C, CH$_{butadiene}$), 123.50 (1 C, CH$_{butadiene}$), 83.59 (1 C, C$_{Cp-ipso}$), 69.71 (C$_{Cp}$), 69.64 (C$_{Cp}$), 67.22 (C$_{Cp}$) ppm. FTIR: $\tilde{v}$ = 3039 (w, br.), 3023 (m, sh), 2956 (w, sh), 2922 (m, sh), 2849 (m, sh), 1897 (w, br.), 1606 (m, sh), 1429 (m, sh), 1409 (m, sh), 1323 (w, sh), 1305 (w, sh), 1260 (m, sh), 1235 (m, sh), 1221 (m, sh), 1133 (m, sh), 1104 (s, sh), 1022 (s, sh), 927 (m, sh), 879 (m, sh), 864 (m, sh), 814 (s, sh), 783 (m, sh), 681 (m, sh), 618 (m, sh), 563 (m, sh) cm^{-1}. EI-MS (200 °C): *m/z* (%) = 186 (100) [C$_{10}$H$_{10}$Fe]$^{+\cdot}$, 486.1055 (63) [M]$^{+\cdot}$ (calcd. 486.1071), 363 (30) [M – 2H]$^{+\cdot}$, 121 (12) [CpFe]$^+$, 300 (9) [M – Fc]$^{+\cdot}$, 421 (6) [M – Cp]$^{+\cdot}$, 56 (4) Fe$^+$.

Ferrocenylethynylcorannulene (3e): Iodocorannulene (**1**, 73 mg, 0.27 mmol, 1 equiv.), potassium *tert*-butoxide (65 mg, 0.53 mmol, 2 equiv.), ethynylferrocene (**2e**, 67 mg, 0.32 mmol, 1.2 equiv.) and tris(dibenzylideneacetone)dipalladium(0) (1 mol-%) were dissolved in anhydrous THF (1.7 mL) and heated for 4 h at 80 °C (a colour change from orange to dark red was observed after several minutes). The reaction mixture was cooled to room temp., dichloromethane (20 mL) was added, and the red solution was washed with water (3× 20 mL). After the solution was dried with sodium sulfate and filtered, evaporation of the solvent afforded a red oil. Silica gel column chromatography with cyclohexane afforded the pure compound as a red solid **3e** (73 mg, 72%) from the fourth fraction, m.p. 208–211 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.99 (AB, ^3J = 8.7 Hz, 2 H, H$_{rim}$), 7.97 (s, 1 H, H$_{rim}$), 7.83–7.75 (m, 6H H$_{rim}$), 4.70 (s, 2 H, H$_{Cp-sub}$), 4.38 (s, 2 H, H$_{Cp-sub}$), 4.36 (s, 5 H, H$_{Cp}$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 136.31 (1 C, C$_{hub}$), 135.97 (1 C, C$_{hub}$), 135.92 (1 C, C$_{hub}$), 135.42 (1 C, C$_{hub}$), 135.17 (1 C, C$_{hub}$), 131.28 (1 C, C$_{spoke}$), 131.21 (1 C, C$_{spoke}$), 131.18 (1 C, C$_{spoke}$), 131.12 (1 C, C$_{spoke}$), 130.75 (1 C, C$_{spoke}$), 130.52 (1 C, CH$_{rim}$), 127.65 (1 C, CH$_{rim}$), 127.56 (1 C, CH$_{rim}$), 127.50 (1 C, CH$_{rim}$), 127.38 (1 C, CH$_{rim}$), 127.27 (1 C, CH$_{rim}$), 127.26 (1 C, CH$_{rim}$), 126.79 (1 C, CH$_{rim}$), 126.30 (1 C, CH$_{rim}$), 122.38 (1 C, C$_{cor-ipso}$), 92.79 (1 C, C$_{ethynyl}$), 84.31 (1 C, C$_{ethynyl}$), 72.18 (2 C, C$_{Cp}$), 70.80 (5 C, C$_{Cp}$), 69.86 (2 C, C$_{Cp}$) ppm. FTIR: $\tilde{v}$ = 3092 (w, sh), 3027 (w, br.), 2921 (m, sh), 2850 (w, sh), 2207 (m, sh), 1621 (w, sh), 1480 (w, sh), 1428 (w, sh), 1408 (m, sh), 1261 (w, sh), 1104 (m, sh), 1047 (m, sh), 999 (m, sh), 923 (m, sh), 879 (s, sh), 819 (s, sh), 762 (m,

sh), 688 (m, sh), 637 (m, sh), 626 (m, sh), 566 (m, sh) cm^{-1}. EI-MS (170 °C): *m/z* (%) = 458.0738 [M]$^{+\cdot}$ (calcd. 458.0759), 337 (24) [M – C$_5$H$_5$Fe]$^{+\cdot}$, 250 (31) [M – C$_{12}$H$_9$Fe]$^{+\cdot}$, 124 [M – C$_{12}$H$_9$Fe]$^{+\cdot}$.

1-Corannulenylethyny-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (3f): Iodocorannulene (**1**, 57 mg, 0.15 mmol, 1 equiv.), potassium *tert*-butoxide (66 mg, 0.54 mmol, 3.6 equiv.) and tris(dibenzylideneacetone)dipalladium(0) (3.5 mol-%) were dissolved in DMF (2 mL), and water was added (0.4 mL). After the mixture was degassed three times, 1-ethynyl-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**2f**, 97 mg, 0.30 mmol, 2 equiv.) was added. The yellow slurry was heated to 80 °C, whereupon it turned from yellow to red and finally to purple, and was stirred at that temperature for 5 h. The solvent was removed, and the residue was subjected to basic alumina (activity level 1) column chromatography with *n*-pentane/toluene (10:1) as solvent. The product was obtained as a dark purple solid (40 mg, 47%); the compound appears nearly black in the solid state, no melting point could be observed up to 300 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.99 (s, 1 H, H$_{rim}$), 7.95 (AB, ^3J = 8.8 Hz, 2 H, H$_{rim}$), 7.46–7.39 (m, 4 H, H$_{rim}$), 7.35 (AB, ^3J = 8.8 Hz, 2 H, H$_{rim}$), 3.26 (s, 1 H, H$_{Cp}$), 2.07 (s, 6 H, CH$_3$), 1.73 (s, 6 H, CH$_3$), 1.67 (s, 6 H, CH$_3$), 1.66 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (175 MHz, C$_6$D$_6$): δ = 136.63 (1 C, C$_{hub}$), 136.44 (1 C, C$_{hub}$), 136.30 (1 C, C$_{hub}$), 135.94 (1 C, C$_{hub}$), 135.20 (1 C, C$_{hub}$), 131.59 (1 C, C$_{spoke}$), 131.47 (1 C, C$_{spoke}$), 131.42 (1 C, C$_{spoke}$), 131.28 (1 C, C$_{spoke}$), 129.95 (1 C, C$_{spoke}$), 129.33 (1 C, C$_{cor-ipso}$), 128.35 (1 C, CH$_{rim}$), 127.99 (1 C, CH$_{rim}$), 127.66 (1 C, CH$_{rim}$), 127.53 (1 C, CH$_{rim}$), 127.42 (1 C, CH$_{rim}$), 127.29 (1 C, CH$_{rim}$), 126.93 (1 C, CH$_{rim}$), 126.50 (1 C, CH$_{rim}$), 123.89 (1 C), 93.88 (1 C, C$_{ethynyl}$), 88.87 (1 C, C$_{ethynyl}$), 82.61 (2 C, C$_{Cp}$) 82.60 (2 C, C$_{Cp}$), 81.54 (2 C, C$_{Cp}$), 81.29 (1 C, C$_{Cp}$), 72.18 (2 C, C$_{Cp}$), 65.49 (1 C, C$_{Cp}$), 11.21 (2 C, CH$_3$), 11.15 (2 C, CH$_3$), 10.21 (2 C, CH$_3$), 9.27 (2 C, CH$_3$) ppm. FTIR: $\tilde{v}$ = 3033 (w, br.), 2962 (w, sh), 2941 (w, sh), 2896 (m, br.), 2851 (w, sh), 2188 (m, sh), 1497 (w, sh), 1421 (w, sh), 1374 (m, sh), 1367 (m, sh), 1323 (m, sh), 1260 (w, sh), 1240 (w, sh), 1221 (m, sh), 1129 (w, sh), 1106 (w, sh), 1028 (m, sh), 951 (m, sh), 872 (m, sh), 831 (s, sh), 815 (m, sh), 751 (m, sh), 685 (m, sh), 652 (m, sh), 627 (m, sh), 618 (m, sh), 595 (m, sh), 587 (m, sh), 556, 536 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 570.2010; found 570.1988.

1,6-Di(1′-neopentylferrocene)-2,5-dimethylcorannulene (6a): 1-Bromo-1′-neopentylferrocene (111 mg, 0.33 mmol, 4 equiv.) was dissolved in THF (3 mL) and cooled to –30 °C. *n*-Butyllithium (0.15 mL, 2.5 M in *n*-hexane, 4.4 equiv.) was added dropwise. The mixture was stirred for 30 min at –30 °C, anhydrous zinc(II) chloride (68 mg, 0.50 mmol, 6 equiv.) was added, and stirring was continued for 30 min at –30 °C and 30 min at room temp. 1,6-Dibromo-2,5-dimethylcorannulene (**4**, 36 mg, 0.08 mmol, 1 equiv.), palladium(II) acetate (2 mol-%) and triphenylphosphane (4 mol-%) were added at once, and the reaction mixture was stirred at 65 °C for 19 h. After removal of the solvent, silica gel column chromatography with *n*-pentane/dichloromethane (3:1) and 1% triethylamine afforded the red **6a** (49 mg, 75%), m.p. 55–57 °C. ^{1}H NMR (700 MHz, CDCl$_3$): δ = 8.07 (AB, ^3J = 8.8 MHz, 4 H, H$_{rim}$), 7.96 (s, 2 H, H$_{rim}$), 4.68 (s, 2 H, H$_{Cp-sub}$), 4.40 (s, 4 H, H$_{Cp-sub}$), 4.24 (s, 2 H, H$_{Cp-sub}$), 4.21 (s, 2 H, H$_{Cp-sub}$), 3.06 (s, 6 H, CH$_3$), 2.35 (s, 4 H, CH$_2$), 0.85 (s, 18 H, CH$_3$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 135.45 (2 C, C$_{ispo}$), 134.36 (2 C, C$_{hub}$), 134.30 (2 C, C$_{hub}$), 133.69 (1 C, C$_{hub}$), 133.36 (2 C, C$_{spoke}$), 131.99 (2 C, C$_{spoke}$), 131.21 (1 C, C$_{spoke}$), 129.47 (2 C, C$_{ipso}$), 127.78 (2 C, CH$_{rim}$), 125.84 (2 C, CH$_{rim}$), 125.36 (2 C, CH$_{rim}$), 86.28 (2 C, C$_{Cp-ipso}$), 84.84 (2 C, C$_{Cp-ipso}$), 72.76 (4 C, C$_{Cp}$), 71.68 (4 C, C$_{Cp}$), 70.15 (4 C, C$_{Cp}$), 69.43 (4 C, C$_{Cp}$), 44.84 (2 C, CH$_2$), 31.83 [2 C, *C*(CH$_3$)$_3$], 29.40 [6 C, C(*C*H$_3$)$_3$], 17.08 (6 C, CH$_3$) ppm. FTIR: $\tilde{v}$ = 3083 (w, br.), 2947 (m, sh), 2904 (m, sh), 2863 (m, sh), 1620 (w, br.), 1463 (m, sh),

1390 (m, sh), 1328 (w, sh), 1262 (w, sh), 1361 (m, sh), 1328 (w, sh), 1262 (m, sh), 1236 (m, sh), 1201 (w, sh) 1147 (w, sh), 1094 (w, sh), 1026 (m, sh), 822 (s, sh), 807 (s, sh), 794 (s, sh), 735 (s, sh), 705 (s, sh), 668 (m, sh), 585 (m, sh), 540 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 786.2611; found 786.2624.

1,6-Bis(ethynylferrocenyl)-2,5-dimethylcorannunlene (6e): 1,6-Dibromo-2,5-dimethylcorannulene (**4**, 30 mg, 0.07 mmol, 1 equiv.) was dissolved in toluene (3 mL) and triethylamine (1.5 mL) in a 25 mL Schlenk flask. After degasification, ethynylferrocene (**2e**, 44 mg, 0.21 mmol, 3 equiv.), palladium(II) acetate (5 mol-%), triphenylphosphane (10 mol-%) and copper(I) iodide (11 mol-%) were added. The reaction mixture was stirred for 24 h at 70 °C. The solvent was removed under vacuum, and the residual red-brown solid was purified by silica gel chromatography with *n*-pentane/dichloromethane (3:1) with 1% triethylamine added. Compound **6e** was obtained as an orange solid (6 mg, 12%), m.p. 282 °C (dec.). ^{1}H NMR (700 MHz, CDCl$_3$): δ = 8.02 (s, 2 H, H$_{rim}$), 7.92 (s, 2 H, H$_{rim}$), 7.84 (s, 2 H, H$_{rim}$), 4.67 (s, 4 H, H$_{Cp-sub}$), 4.34 (s, 4 H, H$_{Cp-sub}$), 4.32 (s, 10 H, H$_{Cp}$), 2.98 (s, 6 H) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 139.26 (2 C, C$_{ipso}$-cor), 135.81 (C, C$_{hub}$), 134.24 (C, C$_{hub}$), 134.12 (C, C$_{hub}$), 131.67 (C, C$_{spoke}$), 130.52 (C, C$_{spoke}$), 127.54 (C, C$_{spoke}$), 126.10 (2 C, CH$_{rim}$), 125.09 (2 C, CH$_{rim}$), 120.25 (2 C, C$_{ipso}$-cor), 97.53 (2 C, C$_{ethynyl}$), 83.07 (2 C, C$_{ethynyl}$), 80.77 (2 C, C$_{ipso}$-Cp), 71.71 (C, C$_{Cp}$), 70.24 (C, C$_{Cp}$), 69.25 (C, C$_{Cp}$), 29.67 (2 C, CH$_3$) ppm. FTIR: $\tilde{v}$ = 2916 (s, sh), 2848 (s, sh), 2203 (w, sh), 1737 (m, sh), 1593 (m, sh), 1466 (m, sh), 1410 (m, sh), 1373 (m, sh), 1240 (m, sh), 1105 (m, sh), 1023 (m, sh), 1003 (m, sh), 913 (m, sh), 875 (m, sh), 825 (s, sh), 792 (s, sh), 718 (s, sh), 691 (m, sh), 585 (m, sh), 529 (s, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 694.1046; found 694.1063.

1,6-Diferrocenyl-2,5-dimethylcorannulene (6g): Ferrocene (170 mg, 0.92 mmol, 4 equiv.) and potassium *tert*-butoxide (10 mg, 0.09 mmol, 0.4 equiv.) were dissolved in THF (10 mL). The solution was cooled to –30 °C, and *n*-butyllithium (0.6 mL, 2.5 M in *n*-hexane, 4.4 equiv.) was added dropwise. Stirring at –30 °C was continued for 20 min. Anhydrous zinc(II) chloride (187 mg, 1.37 mmol, 6 equiv.) was added. The bright orange solution was stirred at –30 °C for 30 min and at room temp. for 30 min. 1,6-Dibromo-2,5-dimethylcorannulene (**4**, 100 mg, 0.23 mmol, 1 equiv.), palladium(II) acetate (4 mol-%) and triphenylphosphane (8 mol-%) were added at once, and the reaction mixture was stirred at 70 °C for 18 h. The solvent was removed, and the resulting solid was purified by silica gel column chromatography with *n*-pentane/dichloromethane (5:1) and 1% triethylamine as solvent. After a second silica gel column chromatography purification with *n*-pentane/dichloromethane (2:1) and 1% triethylamine as solvent, **6g** (10 mg, 7%) was obtained as an analytically pure orange solid, no sharp m.p., sample darkens above 170 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.02 (AB, ^3J = 8.9 Hz, 4 H, H$_{rim}$), 7.92 (s, 2 H, H$_{rim}$), 4.70 (s, 4 H, H$_{Cp-sub}$), 4.48 (s, 4 H, H$_{Cp-sub}$), 4.31 (s, 10 H, H$_{cp}$), 3.01 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 135.55 (2 C, C$_{ispo}$), 134.14 (2 C, C$_{hub}$), 134.41 (1 C, C$_{hub}$), 133.75 (2 C, C$_{hub}$), 131.89 (C$_{spoke}$), 131.81 (2 C, C$_{hub}$), 129.46 (2 C, C$_{hub}$), 129.46 (2 C, C$_{ispo}$), 126.27 (2 C, CH$_{rim}$), 125.91 (2 C, CH$_{rim}$), 125.39 (2 C, CH$_{rim}$), 85.13 (2 C, C$_{Cp-ipso}$), 72.26 (4 C, C$_{Cp}$), 69.91 (10 C, C$_{Cp}$), 67.97 (4 C, C$_{Cp}$), 17.02 (6 C, CH$_3$) ppm. FTIR: $\tilde{v}$ = 2923 (m, br.), 1446 (w, sh), 1406 (w, sh), 1379 (w, sh), 1379 (w, sh), 1344 (w, sh), 1323 (w, sh), 1301 (vw, sh), 1259 (w, sh), 1198 (w, sh), 1104 (m, sh), 1028 (m, sh), 996 (m, sh), 904 (w, sh), 869 (w, sh), 809 (m, sh), 785 (m, sh), 731 (w, sh), 713 (w, sh), 680 (w, sh), 600 (w, sh), 582 (w, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 646.1064; found 646.1094.

1,2-Bis(trifluoromethyl)-4,9-diferrocenylcorannulene (7g): Ferrocene (215 mg, 1.16 mmol, 5 equiv.) and potassium *tert*-butoxide (13 mg,

0.17 mmol, 0.5 equiv.) were combined in a 25 mL Schlenk tube and dissolved in THF (2 mL). The mixture was cooled to –80 °C, and *tert*-butyllithium (0.84 mL, 1.6 M in *n*-hexane, 7.5 equiv.) was added dropwise. The mixture was stirred for 1 h at –30 °C, anhydrous zinc(II) chloride (284 mg, 2.08 mmol, 9 equiv.) was added to the yellow suspension, and stirring was continued for 1 h at –30 °C and 1 h at room temp. 4,9-Dibromo-1,2-bis(trifluoromethyl)corannulene (**5**, 126 mg, 0.23 mmol, 1 equiv.), palladium(II) acetate (4 mol-%) and triphenylphosphane (8 mol-%) were added, and the reaction mixture was stirred at 60 °C for 24 h. The reaction was quenched by dilution with dichloromethane and poured on water. The organic layer was washed with water (4 × 100 mL), dried with sodium sulfate and filtered. The product was purified by silica gel column chromatography with *n*-pentane/dichloromethane (5:1). A deep red solid (14 mg, 8%) was obtained in the second fraction, m.p. 162 °C (dec.). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.41 (s, 2 H, H$_{rim}$), 8.17 (AB, ^3J = 8.9 Hz, 4 H, H$_{rim}$), 4.92–4.53 (m, 8 H, H$_{Cp-subst}$), 4.20 (s, 10 H, H$_{Cp}$) ppm. ^{13}C NMR (176 MHz, CDCl$_3$): δ = 141.42 (2 C, C$_{ipso}$-cor), 136.20 (1 C, C$_{hub}$), 134.66 (2 C, C$_{hub}$), 134.22 (2 C, C$_{hub}$), 130.55 (2 C, C$_{spoke}$), 130.35 (1 C, C$_{spoke}$), 128.43 (2 C, CH$_{rim}$), 127.64 (2 C, CH$_{rim}$), 125.13 (2 C, C$_{spoke}$), 124.57 (2 C, CH$_{rim}$), 70.73 (4 C, C$_{Cp-sub}$), 70.20 (4 C, C$_{Cp-sub}$), 67.97 (2 C, C$_{ipso}$-Cp), 65.84 (10 C, C$_{Cp}$) ppm; the *ipso* carbon atom with trifluoromethyl substituents and the carbon atom of the trifluoromethyl groups could not be observed. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –50.07 (s, 6 F, CF$_3$) ppm. FTIR: $\tilde{v}$ = 2921 (s, sh), 2851 (m, sh), 1737 (w, sh), 1704 (w, sh), 1626 (w, br.), 1462 (w, sh), 1416 (w, sh), 1300 (m, sh), 1264 (s, sh), 1228 (m, sh), 1125 (s, sh), 1067 (m, sh), 1031 (m, sh), 1000 (m, sh), 906 (m, sh), 806 (s, sh), 729 (m, sh), 646 (w, sh), 567 (w, sh) cm^{-1}. EI-MS (250 °C): *m/z* (%) = 745.0498 (100) [M]$^{+\cdot}$ (calcd. 754.0483), 377 (21) [M]$^{2+}$, 614 (11) [C$_{40}$H$_{22}$Fe$_2$]$^{+\cdot}$, 250 (5) [C$_{20}$H$_{10}$]$^{+\cdot}$, 376 (4) [C$_{30}$H$_{16}$]$^{+\cdot}$, 434 (4) [C$_{30}$H$_{18}$Fe]$^{+\cdot}$.

1,2,5,6-Tetra(1′-neopentylferrocenyl)corannulene (9a): *n*-Butyllithium (0.63 mL, 2.5 M in *n*-hexane, 8.8 equiv.) was added dropwise to a solution of 1-bromo-1′-neopentylferrocene (477 mg, 1.42 mmol, 8 equiv.) in THF (5.7 mL). The reaction mixture was stirred at –30 °C for 30 min. Anhydrous zinc(II) chloride (340 mg, 2.49 mmol, 14 equiv.) was added, and stirring was continued for 30 min at –30 °C and for 30 min at room temp. 1,2,5,6-Tetrabromocorannulene (**8**, 100 mg, 0.18 mmol, 1 equiv.), palladium(II) acetate (4 mol-%) and triphenylphosphane (8 mol-%) were added, and the reaction mixture was stirred at 62 °C for 48 h. The solvent was removed under vacuum. Purification by silica gel column chromatography with *n*-pentane/dichloromethane (10:1) and 1% triethylamine as eluent yielded **9a** (87 mg, 38%) from the last (fourth) fraction as a red solid, m.p. 132 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.11 (s, 2 H, H$_{rim}$), 8.49 (AB, ^3J = 8.9 Hz, 4 H, H$_{rim}$), 4.25–4.24 (br m, 8 H, H$_{Cp-sub}$), 4.19–4.18 (m, 8 H, H$_{Cp-sub}$), 3.95–3.91 (m, 16 H, H$_{Cp-sub}$), 2.15 (s, 4 H, CH$_2$), 2.13 (s, 4 H, CH$_2$), 0.72 (s, 18 H, CH$_3$), 0.70 (s, 18 H, CH$_3$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 135.79 (2 C, C$_{hub}$), 135.62 (2 C, C$_{hub}$), 134.45 (2 C, C$_{ispo}$), 134.34 (1 C, C$_{hub}$), 132.93 (2 C, C$_{spoke}$), 130.51 (2 C, C$_{spoke}$), 129.49 (1 C, C$_{spoke}$), 128.70 (2 C, C$_{ispo}$), 128.49 (2 C, CH$_{rim}$), 127.40 (2 C, CH$_{rim}$), 125.49 (2 C, CH$_{rim}$), 86.51 (2 C, C$_{Cp-ipso}$), 86.30 (2 C, C$_{Cp-ipso}$), 86.09 (2 C, C$_{Cp-ipso}$), 86.01 (2 C, C$_{Cp-ipso}$), 73.36 (4 C, C$_{Cp}$), 73.35 (4 C, C$_{Cp}$), 71.61 (4 C, C$_{Cp}$), 71.58 (4 C, C$_{Cp}$), 70.60 (4 C, C$_{Cp}$), 70.50 (4 C, C$_{Cp}$), 69.20 (4 C, C$_{Cp}$), 69.10 (4 C, C$_{Cp}$), 44.88 (2 C, CH$_2$), 44.86 (2 C, CH$_2$), 31.84 [2 C, *C*(CH$_3$)$_3$], 31.82 [2 C, *C*(CH$_3$)$_3$], 29.45 (6 C, CH$_3$), 29.44 (6 C, CH$_3$) ppm. FTIR: $\tilde{v}$ = 3085 (w, br.), 2947 (m, sh), 2904 (m, sh), 2862 (w, sh), 1464 (m, sh), 1389 (w, sh), 1361 (m, sh), 1328 (w, sh), 1234 (m, sh), 1159 (m, sh), 1026 (m, sh), 904 (m, sh), 818 (s, sh), 729 (s, sh), 645 (m, sh),

586 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 1266.3814; found 1266.3900.

1,2,5,6-Tetra(4-ferrocenylphenyl)corannulene (9b): 1-Iodo-4-(ferrocenyl)benzene (274 mg, 0.71 mmol, 8 equiv.) was dissolved in THF (5.7 mL). The solution was cooled to –20 °C, and *n*-butyllithium (0.31 mL, 2.5 M in *n*-hexane, 8.8 equiv.) was added dropwise; stirring at –20 °C was continued for a further 20 min. Anhydrous zinc(II) chloride (169 mg, 1.24 mmol, 14 equiv.) was added, and stirring was continued for 30 min at –20 °C and for 30 min at room temp. 1,2,5,6-Tetrabromocorannulene (**8**, 50 mg, 0.09 mmol, 1 equiv.), palladium(II) acetate (4 mol-%) and triphenylphosphane (8 mol-%) were added, and the reaction mixture was heated at 70 °C for 24 h. The solvent was removed, and silica gel column chromatography with *n*-pentane/dichloromethane (2:1) afforded the orange **9b** (33 mg, 28%) within the last (third) fraction, m.p. darkens above 197 °C. ^{1}H NMR (700 MHz, CD$_2$Cl$_2$): δ = 7.82 (AB, ^3J = 8.7 Hz, 4 H, H$_{rim}$), 7.73 (s, 2 H, H$_{rim}$), 7.47–7.44 (m, 8 H, H$_{phenyl}$), 7.27–7.24 (m, 8 H, H$_{phenyl}$), 4.67 (s, 4 H, H$_{Cp-sub}$), 4.66 (s, 4 H, H$_{Cp-sub}$), 4.32 (s, 4 H, H$_{Cp-sub}$), 4.30 (s, 4 H, H$_{Cp-sub}$), 4.04 (s, 10 H, H$_{Cp}$), 4.02 (s, 10 H, H$_{Cp}$) ppm. ^{13}C NMR (175 MHz, CD$_2$Cl$_2$): δ = 139.51 (C$_{hub}$), 139.29 (C$_{hub}$), 138.42 (2 C, C$_{Ph-ipso}$), 138.39 (2 C, C$_{Ph-ipso}$), 135.84 (1 C, C$_{spoke}$), 135.49 (2 C, C$_{spoke}$), 134.67 (2 C, C$_{spoke}$), 132.31 (4 C, CH$_{Ph}$), 132.28 (4 C, CH$_{Ph}$), 131.27 (2 C, CH$_{rim}$), 130.93 (2 C, CH$_{rim}$), 130.74 (2 C, CH$_{rim}$), 127.85 (2 C, CH$_{rim}$), 127.75 (2 C, CH$_{rim}$), 125.66 (8 C, CH$_{Ph}$), 85.18 (2 C, C$_{Cp-ipso}$), 85.15 (2 C, C$_{Cp-ipso}$), 70.35 (10 C, C$_{Cp}$), 70.33 (10 C, C$_{Cp}$), 69.70 (4 C, C$_{Cp}$), 69.69 (4 C, C$_{Cp}$), 66.99 (4 C, C$_{Cp}$), 66.97 (4 C, C$_{Cp}$) ppm. FTIR: ṽ = 3088 (w, br.), 3026 (w, br.), 2921 (m, sh), 2850 (m, sh), 1607 (m, sh), 1526 (m, sh), 1455 (m, sh), 1387 (w, sh), 1353 (w, br.), 1280 (m, sh), 1186 (w, sh), 1105 (m, sh), 1082 (w, sh), 1054 (w, sh), 1000 (m, sh), 906 (w, sh), 886 (m, sh), 727 (s, sh), 755 (m, sh), 650 (m, sh), 600 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 1290.1936; found 1290.1994.

1,2,5,6-Tetrakis[(*E*)-2-(ferrocenyl)ethenyl]corannulene (9c): 1,2,5,6-Tetrabromocorannulene (**8**, 100 mg, 0.18 mmol, 1 equiv.), vinylferrocene (**2c**, 170 mg, 0.80 mmol, 4.5 equiv.), potassium carbonate (1.11 g, 8 mmol, 45 equiv.), tetra-*n*-butylammonium bromide (1.03 g, 3.20 mmol, 18 equiv.) and palladium(II) acetate (10 mol-%) were suspended in DMF (16 mL). After degasification, the brown slurry was stirred at 80 °C for 48 h. Compound **2c** (170 mg, 0.80 mmol, 4.5 equiv.) and palladium(II) acetate (10 mol-%) were added again, and stirring at 80 °C was continued for 24 h. After the reaction mixture cooled to room temp., dichloromethane (50 mL) was added, and the organic phase was washed with water (4× 150 mL) and dried with sodium sulfate. Silica gel column chromatography with *n*-pentane/dichloromethane (2:1) afforded a red amorphous solid (62 mg), which was again purified by neutral alumina column chromatography with *n*-pentane/toluene (1:1) to yield **9c** as a bright red solid (17 mg, 9%), m.p. 246 °C (dec.). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.14 (s, 2 H, H$_{rim}$), 8.00 (AB, ^3J = 8.9 Hz, 4 H, H$_{rim}$), 7.35–7.14 (m, 8 H, H$_{vinyl}$), 4.65 (s, 8 H, H$_{Cp-sub}$), 4.39 (s, 8 H, H$_{Cp-sub}$), 4.27 (s, 10 H, H$_{Cp}$), 4.26 (s, 10 H, H$_{Cp}$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 135.74 (1 C, C$_{hub}$), 134.82 (2 C, C$_{hub}$), 134.07 (2 C, C$_{hub}$), 131.54 (1 C, C$_{spoke}$), 131.48 (2 C, C$_{spoke}$), 131.33 (2 C, C$_{spoke}$), 128.01 (2 C, C$_{rim}$), 126.94 (2 C, C$_{rim}$), 126.57 (2 C, C$_{rim}$), 124.89 (2 C, C$_{rim}$), 124.72 (2 C, C$_{rim}$), 98.56 (2 C, C$_{vinyl}$), 98.42 (2 C, C$_{vinyl}$), 84.11 (2 C, C$_{vinyl}$), 84.01 (2 C, C$_{vinyl}$), 72.01 (4 C, C$_{Cp}$), 70.46 (20 C, C$_{vinyl}$), 69.52 (4 C, C$_{vinyl}$), 65.33 (2 C, C$_{Cp-ispo}$) ppm. FTIR: ṽ = 3091 (m, br.), 3035 (w, sh), 2919 (m, sh), 2849 (m, sh), 2919 (s, sh), 2849 (m, sh), 2191 (m, sh), 1728 (m, sh), 1680 (w, sh), 1613 (m, sh), 1511 (w, br.), 1461 (m, sh), 1409 (m, sh), 1375 (m, sh), 1260 (m, sh), 1239 (m, sh), 1183 (w, sh), 1104 (m, sh), 1043 (m, sh), 1027 (m, sh), 1002 (m, sh), 997 (m, sh),

927 (m, sh), 878 (w, sh), 810 (s, sh), 726 (m, sh), 695 (m, sh), 656 (m, sh), 629 (w, sh), 593 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]+ 1090.1310; found 1090.1385.

1,2,5,6-Tetra(ferrocenylethynyl)corannulene (9e): 1,2,5,6-Tetrabromocorannulene (**8**, 100 mg, 0.19 mmol, 1.0 equiv.), ethynylferrocene (**2e**, 163 mg, 0.78 mmol, 4.4 equiv.), copper(I) iodide (8 mg, 0.04 mmol, 0.2 equiv.), palladium(II) acetate (10 mol-%) and triphenylphosphane (20 mol-%) were dissolved in a mixture of toluene (10 mL) and triethylamine (5 mL). After degasification, the brown solution was stirred at 70 °C for 20 h. The red-brown reaction mixture was transferred to a separating funnel with dichloromethane (20 mL) and washed with water (3× 100 mL) and brine (1× 50 mL). The organic layer was dried with anhydrous sodium sulfate and filtered, and the solvent was removed. Silica gel column chromatography was conducted with *n*-pentane/dichloromethane (2:1). The product was obtained in the last fraction as a deep red solid (81 mg, 42%), m.p. 225.0 °C. ^{1}H NMR (700 MHz, CD$_2$Cl$_2$): δ = 8.12 (s, 2 H, H$_{rim}$), 7.97 (AB, ^3J = 8.7 Hz, 4 H, H$_{rim}$), 4.73 (s, 8 H, C$_{Cp-sub}$), 4.37 (s, 8 H, C$_{Cp-sub}$) 4.32 (s, 20 H, C$_{Cp}$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 135.75 (1 C, C$_{hub}$) 134.82 (2 C, C$_{hub}$), 134.07 (2 C, C$_{hub}$), 131.54 (1 C, C$_{spoke}$), 131.48 (2 C, C$_{spoke}$), 131.33 (2 C, C$_{spoke}$), 128.01 (2 C, CH$_{rim}$), 129.94 (2 C, CH$_{rim}$), 126.58 (2 C, CH$_{rim}$), 124.89 (2 C, C$_{ipso}$), 124.72 (2 C, C$_{ipso}$), 98.57 (2 C, C$_{ethynyl}$), 98.42 (2 C, C$_{ethynyl}$), 84.11 (2 C, C$_{ethynyl}$), 84.01 (2 C, C$_{ethynyl}$), 72.01 (8 C, C$_{Cp-sub}$), 70.45 (20 C, C$_{Cp}$), 69.52 (8 C, C$_{Cp-sub}$), 65.33 (4 C, C$_{Cp-ipso}$) ppm. FTIR: ṽ = 3087 (w, sh), 3048 (w, sh), 2953 (w, sh), 2924 (m, sh), 2847 (w, sh), 2250 (w, sh), 2187 (m, sh), 773 (w, sh), 1628 (m, br.), 1470 (m, sh), 1405 (m, sh), 1386 (m, sh), 1341 (m, sh), 1260 (m, sh), 1199 (m, sh), 1185 (m, sh), 1102 (m, sh), 1045 (m, sh), 1025 (m, sh), 998 (s, sh), 948 (w, sh), 905 (m, sh), 810 (s, sh), 726 (s, sh), 674 (m, sh), 647 (m, sh), 600 (m, sh), 579 (m, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 1082.0684; found 1082.0611.

1,2,5,6-Tetra(1′,2,2′,3,3′4,4′,5-octamethylferrocenyl)corannulene (9f): 1,2,5,6-Tetrabromocorannulene (**8**, 70 mg, 0.12 mmol, 1 equiv.), 1-ethynyl-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**2f**, 175 mg, 0.54 mmol, 4.4 equiv.), palladium(II) acetate (5 mol-%), triphenylphosphane (10 mol-%) and copper(I) iodide (5 mol-%) were dissolved in diisopropylamine (1.2 mL). After freeze–pump–thaw cycling, the mixture was heated to 80 °C, whereupon it turned from a brown to a purple solution, which was stirred at that temperature for 56 h. After removal of the solvent, the dark purple solid was subjected to basic alumina column chromatography (activity level 1) with *n*-pentane/toluene (3:1) as solvents to afford **9f** (72 mg, 40%). The compound is a black solid, and no melting point could be observed up to 300 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.60 (s, 2 H, H$_{rim}$), 8.01 (AB, ^3J = 8.8 Hz, 4 H, H$_{rim}$), 3.34 (s, 4 H, H$_{Cp}$), 2.31 (s, 12 H, CH$_3$), 2.10 (s, 12 H, CH$_3$), 1.78 (s, 12 H, CH$_3$), 1.17 (s, 12 H, CH$_3$), 1.69 (s, 12 H, CH$_3$) ppm. ^{13}C NMR (175 MHz, C$_6$D$_6$): δ = 137.90 (1 C, C$_{hub}$), 136.42 (1 C, C$_{ipso}$), 135.24 15 (2 C, C$_{hub}$), 134.55 (2 C, C$_{hub}$), 132.38 (2 C, C$_{spoke}$), 132.21 (2 C, C$_{spoke}$), 131.58 (1 C, C$_{spoke}$), 128.57 (2 C, C$_{rim}$), 127.38 (2 C, C$_{rim}$), 126.74 (2 C, C$_{rim}$), 125.67 (2 C, C$_{rim}$), 125.56 (2 C, C$_{rim}$), 99.60 (2 C, C$_{ethynyl}$), 99.37 (2 C, C$_{ethynyl}$), 88.89 (2 C, C$_{ethynyl}$), 88.62 (2 C, C$_{ethynyl}$), 82.81 (C, C$_{Cp}$), 82.78 (C, C$_{Cp}$), 81.51 (C, C$_{Cp}$), 81.46 (C, C$_{Cp}$), 81.39 (C, C$_{Cp}$), 81.36 (C, C$_{Cp}$), 81.09 (C, C$_{Cp}$), 81.05 (C, C$_{Cp}$), 66.38 (C, C$_{Cp}$), 66.28 (C, C$_{Cp}$), 11.54 (2 C, CH$_3$), 11.50 (2 C, CH$_3$), 11.33 (2 C, CH$_3$), 11.31 (2 C, CH$_3$), 10.22 (2 C, CH$_3$), 10.20 (2 C, CH$_3$), 9.43 (2 C, CH$_3$), 9.40 (2 C, CH$_3$) ppm. FTIR: ṽ = 3056 (w, sh), 2964 (m, sh), 2942 (m, sh), 2899 (s, sh), 2854 (m, sh), 2176 (s, sh), 1611 (w, sh), 1444 (m, sh), 1373 (s, sh), 1328 (s, sh), 1261 (w, sh), 1083 (w, sh), 970 (w, sh), 822 (m, sh), 728 (m, sh), 651 (w, sh),

571 (w, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 1531.5770; found 1531.5724; calcd. for [M]$^{2+}$ 765.7885; found 765.7833.

1,2,5,6-Tetra(ferrocenyl)corannulene (9g): Ferrocene (265 mg, 1.42 mmol, 8 equiv.) and potassium *tert*-butoxide (16 mg, 0.14 mmol, 0.8 equiv.) were dissolved in THF (4 mL). The solution was cooled to –30 °C, and *tert*-butyllithium (1.12 mL in *n*-hexane, 2.34 mmol, 12 equiv.) was added dropwise. The mixture was stirred for 1 h at the same temperature, and anhydrous zinc(II) chloride (340 mg, 2.49 mmol, 14 equiv.) was added. The orange reaction mixture was stirred for a further 30 min at –30 °C and 30 min at room temp. Palladium(II) acetate (4 mol-%), triphenylphosphane (8 mol-%) and 1,2,5,6-tetrabromocorannulene (**8**, 100 mg, 0.19 mmol, 1 equiv.) were added, and the reaction mixture was stirred at 60 °C for 48 h. After the addition of water (2 mL), the reaction mixture was extracted with dichloromethane (20 mL). The organic layer was washed with water (3 × 50 mL), dried with anhydrous sodium sulfate and filtered, and the solvent was removed under vacuum. After silica gel column chromatography with *n*-pentane/dichloromethane (2:1) as eluent, the red product was obtained in the second fraction. After removal of the solvent, a red amorphous solid was obtained (108 mg, 57%), m.p. 254 °C (dec.). ^{1}H NMR (700 MHz, CD$_2$Cl$_2$): δ = 9.12 (s, 2 H, H$_{rim}$), 8.48 (AB, ^3J = 8.9 Hz, 4 H, H$_{rim}$), 4.30 (br s, 20 H, H$_{Cp}$), 4.04 (s, 8 H, H$_{Cp-sub}$), 4.00 (s, 8 H, H$_{Cp-sub}$) ppm. ^{13}C NMR (175 MHz, CDCl$_3$): δ = 136.39 (2 C, C$_{ipso}$), 136.06 (2 C, C$_{ipso}$), 134.64 (1 C, C$_{hub}$), 134.45 (2 C, C$_{hub}$), 133.53 (2 C, C$_{hub}$), 130.93 (2 C, C$_{spoke}$), 129.88 (2 C, C$_{spoke}$), 129.31 (1 C, C$_{spoke}$), 128.64 (2 C, CH$_{rim}$), 128.09 (2 C, CH$_{rim}$), 126.12 (2 C, CH$_{rim}$), 87.40 (2 C, C$_{Cp-ipso}$), 86.75 (2 C, C$_{Cp-ipso}$), 73.42 (4 C, C$_{Cp-sub}$), 73.34 (4 C, C$_{Cp-sub}$), 70.40 (10 C, C$_{Cp}$), 70.37 (10 C, C$_{Cp}$), 68.12 (4 C, C$_{Cp-sub}$), 68.10 (4 C, C$_{Cp-sub}$) ppm. FTIR: ṽ = 3039 (m, sh), 2960 (m, sh), 2849 (m, sh), 1732 (m, br.), 1680 (w, br.), 1619 (m, sh), 1436 (m, sh), 1409 (m, sh), 1380 (w, sh), 1328 (m, sh), 1298 (m, sh), 1258 (m, sh), 1221 (w, sh), 1104 (m, sh), 1027 (s, sh), 1000 (s, sh), 873 (m, sh), 812 (s, sh), 799 (s, sh), 733 (s, sh), 701 (s, sh), 672 (m, sh), 640 (m, sh), 582 (m, sh) cm^{-1}. EI-MS (300 °C): *m/z* (%) = 732 (100) [C$_{45}$H$_{24}$Fe$_3$]$^{+}$, 986 (82) [M]$^{+}$, 614 (71) [C$_{40}$H$_{22}$Fe$_2$]$^+$, 558 (52) [C$_{40}$H$_{17}$Fe$_2$]$^+$, 186 (40) [C$_{10}$H$_{10}$Fe]$^+$, 367 (10) [C$_{45}$H$_{24}$Fe$_3$]$^{2+}$. HRMS (ESI): calcd. for [M]$^+$ 986.0684; found 986.0678.

1,3,5,7,9-Penta(1′-neopentylferrocenyl)corannulene (11a): 1-Bromo-1′-neopentylferrocene (317 mg, 0.95 mmol, 10 equiv.) was dissolved in THF (2 mL). After the solution was cooled to –30 °C, *n*-butyllithium (0.46 mL, 2.5 M in *n*-pentane, 12 equiv.) was added dropwise, and the red suspension was stirred for 30 min at –30 °C. After the addition of anhydrous zinc(II) chloride (194 mg, 1.42 mmol, 15 equiv.) in THF (2 mL), stirring at –30 °C was continued for 1 h at –30 °C and 1 h at room temp. 1,3,5,7,9-Pentachlorocorannulene (**10**, 40 mg, 0.09 mmol, 1 equiv.) and dichloro[1,3-bis(diphenylphosphanyl)propane]nickel (17 mg, 0.03 mmol, 0.3 equiv.) were added, and the reaction mixture was stirred at 60 °C for 3 d. The solvent was removed and preparative TLC on silica gel with *n*-hexane/dichloromethane (3:1) afforded the target product as a red solid (22 mg, 15%), m.p. 137 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.51 (s, 5 H, H$_{rim}$), 4.87–4.86 (m, 10 H, H$_{Cp-sub}$), 4.41–4.40 (m, 10 H, H$_{Cp-sub}$), 4.18–4.16 (m, 10 H, H$_{Cp-sub}$), 4.15–4.14 (m, 10 H, H$_{Cp-sub}$), 2.26 (s, 10 H, CH$_2$), 0.78 (s, 45 H, CH$_3$) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 138.53 (5 C, C$_{cor}$), 134.51 (5 C, C$_{cor}$), 128.90 (5 C, C$_{cor}$), 125.15 (5 C, C$_{cor}$), 86.85 (5 C, C$_{Cp-ipso}$), 86.10 (5 C, C$_{Cp-ipso}$), 72.03 (10 C, C$_{Cp}$), 70.30 (10 C, C$_{Cp}$), 70.08 (10 C, C$_{Cp}$), 70.06 (10 C, C$_{Cp}$), 44.90 (5 C, CH$_2$), 31.94 [5 C, *C*(CH$_3$)$_3$], 29.52 (15 C, CH$_3$) ppm. FTIR: ṽ = 3086 (w, br.), 2948 (m, sh), 2948 (m, sh), 2863 (m, sh), 1627 (w, br.), 1464 (m, sh), 1309 (m, sh), 1361 (m, sh), 1330 (w, sh), 1235 (m, sh), 1160 (w, sh), 1141 (m, sh), 1027

(m, sh), 941 (m, sh), 877 (m, sh), 817 (s, sh), 754 (m, sh), 633 (w, sh), 614 (w, sh) cm^{-1}. HRMS (ESI): calcd. for [M]$^+$ 1521.4604; found 1521.4606.

1,3,5,7,9-Pentaferrocenylcorannulene (11g): Ferrocene (264 mg, 1.42 mmol, 15 equiv.) and potassium *tert*-butoxide (16 mg, 0.14 mmol, 1.5 equiv.) were dissolved in THF (2 mL). The red solution was cooled to –30 °C, and *tert*-butyllithium (0.87 mL, 1.6 M in *n*-pentane, 15 equiv.) was added dropwise. The mixture was stirred at the same temperature for 1 h, and a red precipitate was observed. Anhydrous zinc(II) chloride (258 mg, 1.89 mmol, 20 equiv.) in THF (3 mL) was added. The mixture was stirred at –30 °C for 30 min and r.t. for 30 min, and 1,3,5,7,9-pentachlorocorannulene (**10**, 40 mg, 0.09 mmol, 1 equiv.) and dichloro[1,3-bis(diphenylphosphanyl)propane]nickel (17 mg, 0.03 mmol, 0.3 equiv.) were added; the reaction mixture was stirred at 67 °C for 29 h. The reaction mixture was transferred to a 50 mL one-neck flask. The solvent was removed, and the red solid residue was sonicated with *n*-hexane (3 × 20 mL). The remaining residue was filtered through silica gel with *n*-hexane, to remove apolar residues, and then *n*-hexane/dichloromethane (1:1). Finally, preparative TLC on silica gel with *n*-pentane/dichloromethane (1:1) afforded the analytically pure product (4.5 mg, 6%), m.p. 194 °C. ^{1}H NMR (700 MHz, CDCl$_3$): δ = 8.57 (s, 5 H, H$_{rim}$), 4.99 (s, 10 H, H$_{Cp-sub}$), 4.56 (s, 10 H, H$_{Cp-sub}$), 4.32 (s, 50 H, H$_{Cp}$) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 138.31 (5 C, C$_{cor}$), 134.44 (5 C, C$_{cor}$), 128.64 (5 C, C$_{cor}$), 125.07 (5 C, C$_{cor}$), 86.08 (5 C, C$_{Cp-ipso}$), 70.00 (25 C, C$_{Cp}$), 69.45 (10 C, C$_{Cp-sub}$), 69.16 (25 C, C$_{Cp-sub}$) ppm. FTIR: ṽ = 3090 (m, br.), 2919 (m, sh), 2850 (m, sh), 2244 (w, br.), 1731 (m, sh), 1612 (w, sh), 1479 (m, sh), 1462 (m, sh), 1412 (m, sh), 1378 (w, sh), 1251 (m, sh), 1163 (w, sh), 1106 (m, sh), 1051 (m, sh), 1024 (m, sh), 1000 (m, sh), 956 (w, sh), 905 (m, sh), 863 (w, sh), 814 (s, sh), 726 (s, sh), 448 (mid, sh) cm^{-1}. MALDI-MS: see Supporting Information.

CCDC-999863 (for **3b**) and -999862 (for **9b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal Structures, computational details, UV/Vis spectra, electrochemistry, MALDI-MS spectrum of **11g**, NMR Spectra.

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