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1,1′-Diaryl-Substituted Ferrocenes: Up to Three Hinges in Oligophenyleneethynylene-Type Molecular Wires

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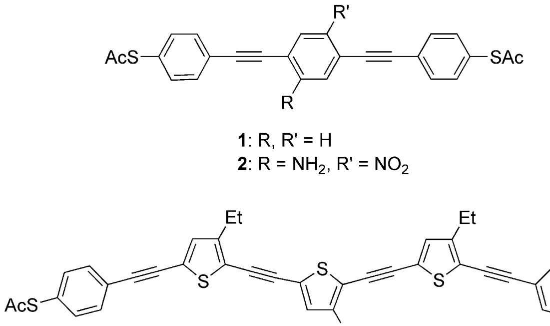
Molecular wires of the oligophenyleneethynylene (OPE)-type are potentially rigid entities. The idea of the work reported herein was to replace some, not all, of the phenylene moieties with ferrocene units, thereby introducing limited conformational flexibility with the ferrocene units acting as hinges as a consequence of the facile rotation around the Cp–Fe–Cp axis. In this context, the syntheses of a number of 1,1′-diaryl-disubstituted ferrocene building blocks are described. The new terminal diynes **22** and **24** were used to construct the first representatives of ferrocene-based molecular wires with three ferrocene hinges. The study includes an X-ray structure analysis of the thiophene-based diyne **24** as well as cyclovoltammetric analyses of a number of the compounds prepared.

Introduction

The continuing miniaturization of electronic devices has triggered the field of molecular electronics in which molecular entities take over the role of electronic devices on the smallest possible level.[1–6] Within this field various electronic wires have been developed, among which oligophenyleneethynylenes (OPEs) and related thiophene-derived compounds such as **1**–**3** are particularly common (Scheme 1).[1,3,6,7] Such compounds often bear so-called "alligator clips" at their ends. In most cases these are thioacetyl or *tert*-butylsulfanyl groups,[1,8] which facilitate the attachment of the wire to a surface, in most cases gold.



Scheme 1. Common molecular wires.

Molecular wires of OPEs and related types are comparatively rigid entities with extended π systems. Possible problems associated with these wires are the π–π stacking of molecular wires as well as their given length, which may or may not satisfy the geometrical demands of a device. Three-dimensional systems with a limited conformational flexibility may be able to adjust their shape to the geometric requirements. However, such systems have been investigated to a much lesser extent.

We, as well as others, have attempted to resolve these issues by replacing some, not all, of the 1,4-phenylene or 2,5-thiophenylene units by 1,1′-ferrocenylene moieties.[9–13] A precondition for this development is the possibility of electron-transfer through the ferrocene unit along a molecular wire. Such conductivity has recently been established by Engtrakul and Sita[12,13] as well as by Dong and coworkers[14,15] and is presumably a result of the redox activity of ferrocene.[16] The ferrocene subunits render the wire three-dimensional and thereby make π–π stacking less likely. In addition, the energy of activation for rotation of the cyclopentadienyl (Cp) ligands in ferrocene around the Cp–Fe–Cp axis is very low[17] (ca. 4 kJ/mol in the gas phase[18]) and thus the ferrocene moieties can act as hinges, which results in a limited conformational flexibility of the wire comparable to that of a foldable ruler. For steric reasons, the rotational barriers in substituted ferrocenes are somewhat higher than in the unsubstituted ferrocene. For example, Okuda and Herdtweck estimated the rotational barrier in 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene to be around 46 kJ/mol,[19] whereas Luke and Streitwieser reported the barrier for 1,1′,3,3′-tetra-*tert*-butylferrocene to be as high as 55 kJ/mol.[20] These numbers clearly indicate that highly substituted ferrocenes have a considerably higher energy of activation for Cp–Fe–Cp rotation than the parent compound. However, these examples have four branched substituents at the cyclopentadienyl ligands, whereas the compounds envisaged by us have only two and are thus sterically less encumbered, although the chains attached are longer. Therefore we expect that the activation energy for Cp–Fe–Cp rotation is a similar order of magni-

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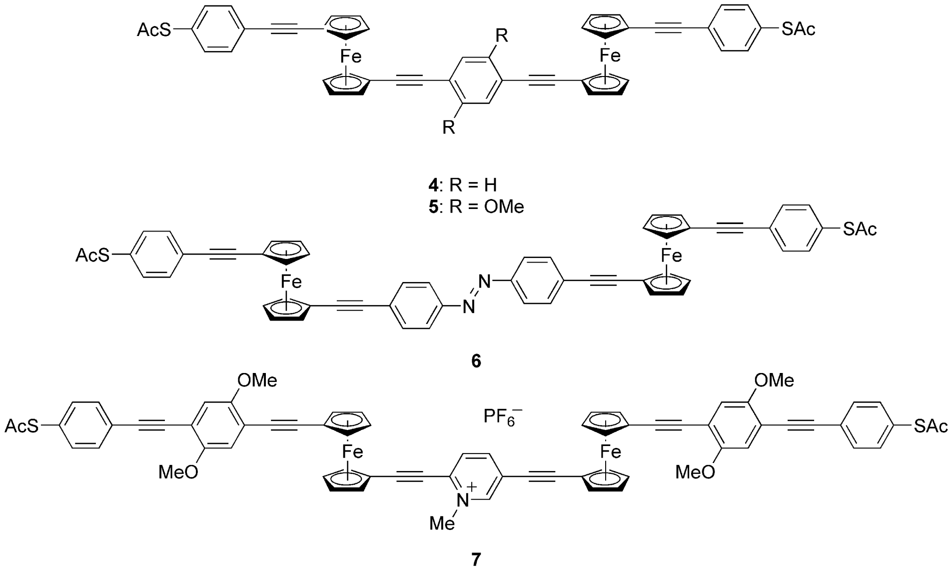


Scheme 2. Ferrocene-based molecular wires.

tude to those of the reported branched representatives; we expect the envisaged rotation to be possible, albeit at a lower rate than in the unsubstituted ferrocene. Compounds **4**–**7** are examples of known ferrocene-based molecular wires (Scheme 2).[10,13]

Molecular wires such as **4**–**7** are usually prepared by palladium-catalyzed coupling reactions of a small number of building blocks. A common building block in this context is 1,1′-bis(trimethylsilylethynyl)ferrocene,[21] which is used as a substitute for the unprotected 1,1′-diethynylferrocene, which is known to be unstable.[22] Problems associated with the use of 1,1′-dialkynylferrocenes include the facile formation of [4]ferrocenophane derivatives as a result of nucleophilic attack, for example, by phenols.[21,23,24]

As an alternative to ferrocene-based molecular wires with triple bonds directly attached to the ferrocene moieties, we envisaged phenylogous derivatives bearing 1,4-phenylene or 2,5-thiophenylene groups attached to the ferrocene with alligator clips or alkynyl groups bound to these. In comparison with 1,1′-dialkynylferrocenes, these compounds are presumably less prone to ferrocenophane formation. Herein we report the synthesis and characterization of some new compounds of this type, including the first ones with up to three ferrocene hinges.

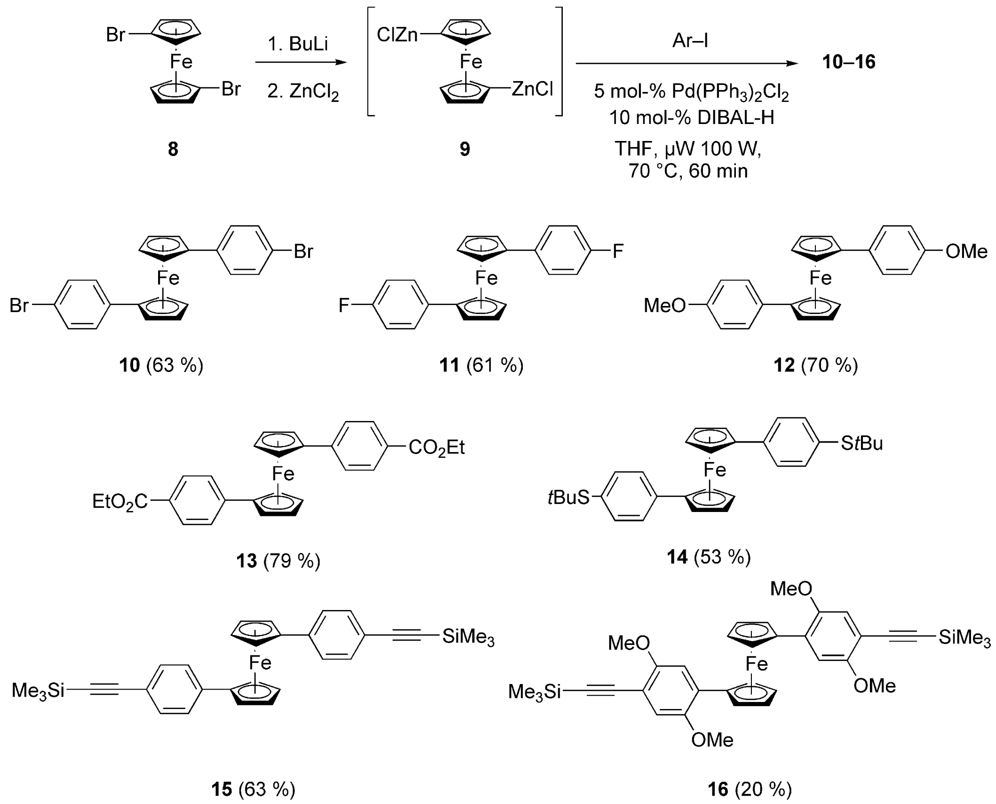
Results and Discussion

Some 1,1′-diarylated ferrocenes have been prepared by Suzuki–Miyaura coupling of ferrocene-1,1′-diboronic acid with bromoarenes,[25] by treatment of substituted cyclopentadienides with $FeCl_2$,[26] or by electrophilic substitution of ferrocene with diazonium salts.[27] However, in the 1,1′-diarylation of ferrocene these procedures suffer either from low yields or reaction times as long as 6 d in the case of the Suzuki–Miyaura coupling reactions. In the search for more practical paths to these compounds we tested the Negishi coupling reaction under microwave irradiation. 1,1′-Dibromoferrocene (**8**)[28,29] was treated with butyllithium followed by zinc chloride to give the corresponding 1,1′-dizincated ferrocene **9**, which underwent Negishi coupling reactions with iodoarenes in the presence of 5 mol-% of $[Pd(PPh_3)_2Cl_2]$ and 10 mol-% of diisobutylaluminium hydride (DIBAL-H) under microwave irradiation to give 1,1′-diarylferrocenes **10**–**16** in good yields in a reaction time of only 60 min (Scheme 3).

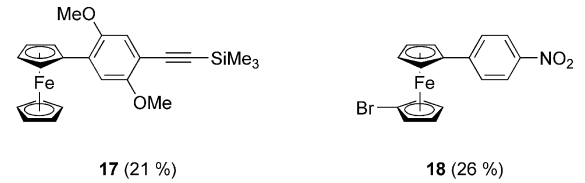
The 63 and 61% yields of the dibromide **10** and the difluoride **11**, respectively, compare with yields of 60 and 45% obtained by the corresponding Suzuki–Miyaura coupling reactions.[25] Compounds **12** and **13** were previously obtained by Broadhead and Pauson by electrophilic substitution in 7 and 26% yields, respectively.[27] Compounds **14**–**16** are new compounds and were characterized spectroscopically. Whereas **10**–**15** were the only reaction products obtained, **16** was formed in a low yield along with the monosubstitution/reduction product **17**, which was obtained in 21% yield. Use of 1-iodo-4-nitrobenzene under the reaction conditions gave only the monosubstitution product **18** (16% yield), which suggests incomplete zincation in addition to a poor yield of the coupling product (Scheme 4).

Thiophene-based molecular wires are of interest in the context of molecular electronics.[1,3,6,7] Therefore we attempted the Negishi coupling reaction of 1,1′-dibromoferrocene with 2-bromo-5-iodothiophene and 2-bromo-5-(trimethylsilylethynyl)thiophene under the usual reaction conditions. Whereas the first reaction gave the disubstitution product **19** exclusively, albeit in poor yield (11%), **20** was obtained in the second reaction in 42% yield along with the monosubstitution/reduction product **21** (8%; Scheme 5).

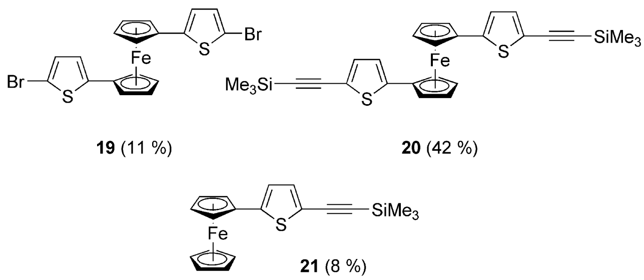
Dibromides **10** and **19** are of interest as building blocks for the synthesis of more extended systems such as new molecular wires. For example, it was possible to prepare **15** by the Sonogashira coupling reaction of **10** with trimethylsilyl-



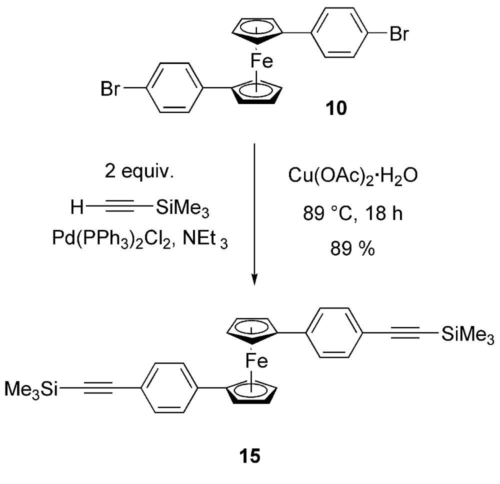
Scheme 3. Synthesis of 1,1′-diarylferrocenes **10**–**16**.



Scheme 4. Monoarylation products **17** and **18**.



Scheme 5. 2-Thiophenyl-substituted ferrocenes **19**–**21**.

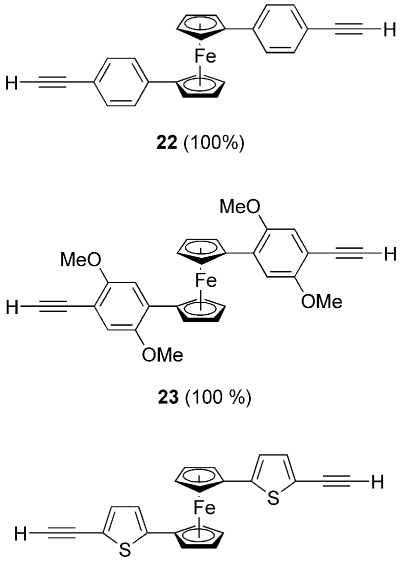


Scheme 6. Sonogashira dialkynylation of **10**.

ethyne in 89% yield. However, taking the yield of the formation of **10** into account, the Negishi route provides a better access to **15**. Attempts to perform the Sonogashira coupling reaction under microwave irradiation gave **15** in only 51% yield along with a small amount of the monosubstitution product (Scheme 6).

Bis(trimethylsilylethynyl)-substituted derivatives **15**, **16**, and **20** undergo protiodesilylation on treatment with K_2CO_3/MeOH or with tetrabutylammonium fluoride in dichloromethane to afford terminal alkynes **22**–**24** in very high yields as air-stable compounds (Scheme 7).

In addition to the usual spectroscopic characterization of the new compounds, we were able to obtain crystals of **24** from dichloromethane/petroleum ether that were suitable for X-ray crystal analysis (Figure 1). The crystal structure analysis shows an eclipsed conformation with the thiophene



22 (100%)

23 (100 %)

24 (92 %)

Scheme 7. Protiodesilylation products **22**–**24**.

rings almost parallel to one another and the sulfur atoms in opposite positions rendering the structure chiral in contrast to a *meso* conformation in which the sulfur atoms are on the same side. The distance between the centers of the cyclopentadienyl rings is 330.7 pm, which is virtually the same distance as in unsubstituted ferrocene (332 pm). The thiophene rings are bent away from each other by about 6° relative to the cyclopentadienyl planes resulting in a distance of 374.6 pm between the centers of the thiophene rings.

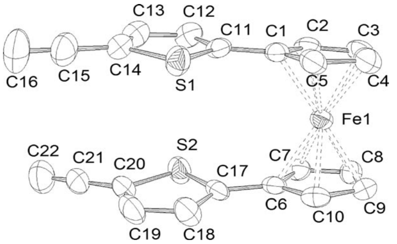


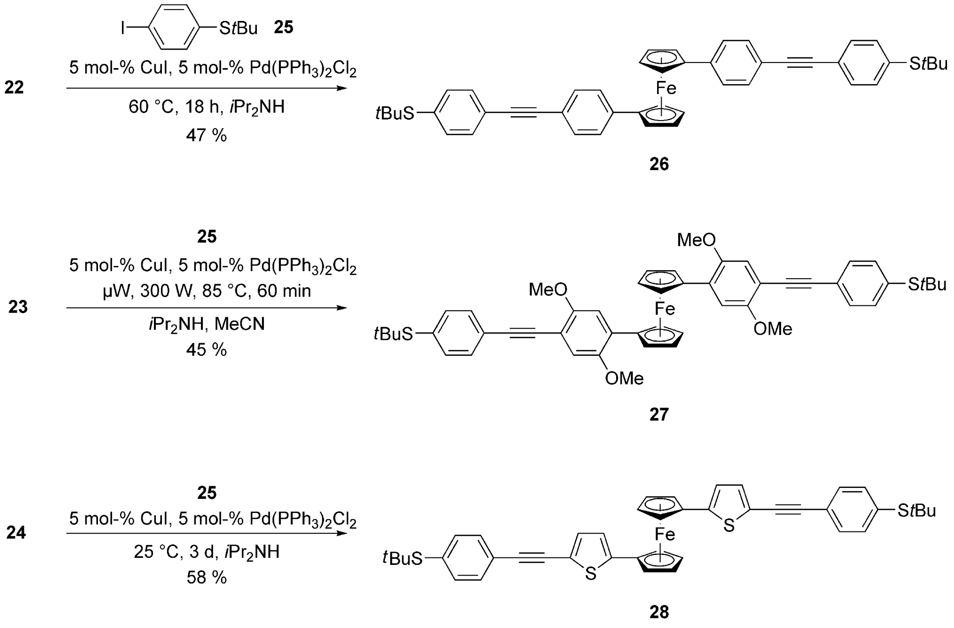
Figure 1. Structure of the the crystal structure of **24**.[30] Selected bond lengths [pm], angles [°] and torsional angles [°]: C1–C2 141.1(4), C1–C5 141.7(5), C1–C11 146.8(4), C2–C3 140.7(5), C3–C4 141.3(6), C4–C5 140.5(5), C6–C7 142.2(5), C6–C10 142.6(4), C6–C17 147.3(4), C7–C8 140.9(4), C8–C9 138.3(6), C9–C10 142.5(4), C14–C15 142.0(5), C15–C16 116.7(5), C20–C21 142.7(5), C21–C22 116.7(5); C14–C15–C16 176.9(5), C20–C21–C22 178.7(4); C2–C1–C11–C12 –5.52, C10–C6–C17–C18 –6.83.

The eclipsed conformation is remarkable because it is counterintuitive with respect to possible steric interactions of the substituents. However, the structure reflects the conformation in the solid state and thus packing effects should also be considered in addition to an attractive π–π interaction between the two thiophenyl substituents. Other 1,1′-disubstituted ferrocene derivatives with similar eclipsed conformations in the solid state include [{C_5Me_4(4-ClC_6H_4)}$_2$Fe],[31] [{C_5Me_4(4-$MeOC_6H_4$)}$_2$Fe],[31] 1,1′-dicyanoferrocene,[32] and a triferrocenyldialkyne.[33] The importance of the eclipsed conformations of 1,1′-disubstituted ferrocenes is, however, documented by the facile formation of [4]ferrocenophanes from 1,1′-dialkynylferrocenes.[21,23,24] Another remarkable feature of the structure is the almost perfect coplanarity of the cyclopentadienyl and thiophene rings with a deviation from coplanarity of only 5–7°, which indicates that the conjugation will not be interrupted by a significant torsion between the thiophenylene and ferrocene substructures. The question that arises is to what extent is such a coplanar conformation possible in the corresponding 1,1′-diarylferrocenes; published structures show some deviation from coplanarity for 1,1′-diphenylferrocene (no torsional angles given).[31] In contrast, trimetallic representatives in which phenyl rings coordinated to $Cr(CO)_3$[34] or $Mn(CO)_3^+$[35] are eclipsed, nearly coplanar conformations were reported, which clearly indicates that steric interactions between the *ortho* protons of the aryl substituent and those of the cyclopentadienyl ligand do not prevent coplanarity. In any case, one has to take into account the fact that the conformations observed in the solid state do not necessarily reflect those in solution or in an electronic device. However, they indicate that coplanarity is possible.

Terminal dialkynes **22**–**24** were subjected to double Sonogashira coupling reactions with *tert*-butyl(4-iodophenyl)sulfane (**25**),[10] which afforded the new molecular wires **26**–**28** in 45–58% yields (Scheme 8). Remarkably, performing the Sonogashira coupling of **22** under microwave irradiation (30 W, 85 °C, 60 min) gave **26** in a reduced yield of only 28%. All the spectroscopic data of the new compounds are in accord with the assigned structures.

Derivatives **16**, **23**, and **27** bear hydroquinone methyl ether subunits and deserve special interest because of the possibility of ether cleavages and the formation of the corresponding hydroquinone derivatives. Such ether cleavages might not only be realized by Lewis acids such as BCl_3, which would presumably give rise to undesired side-reactions, but also under reducing reaction conditions with L-Selectride.[36,37] As redox-active systems the corresponding hydroquinone/quinone subunits would be conjugated to the ferrocene hinges, which are also redox-active, and therefore allow electronic interactions to be observed by cyclic voltammetry. Although the proximity of the methoxy groups to the ferrocene hydrogen atoms might lead to some deviation from coplanarity, this is expected to be less so in the demethylated hydroquinone or quinone products. Investigations along these lines are currently underway.

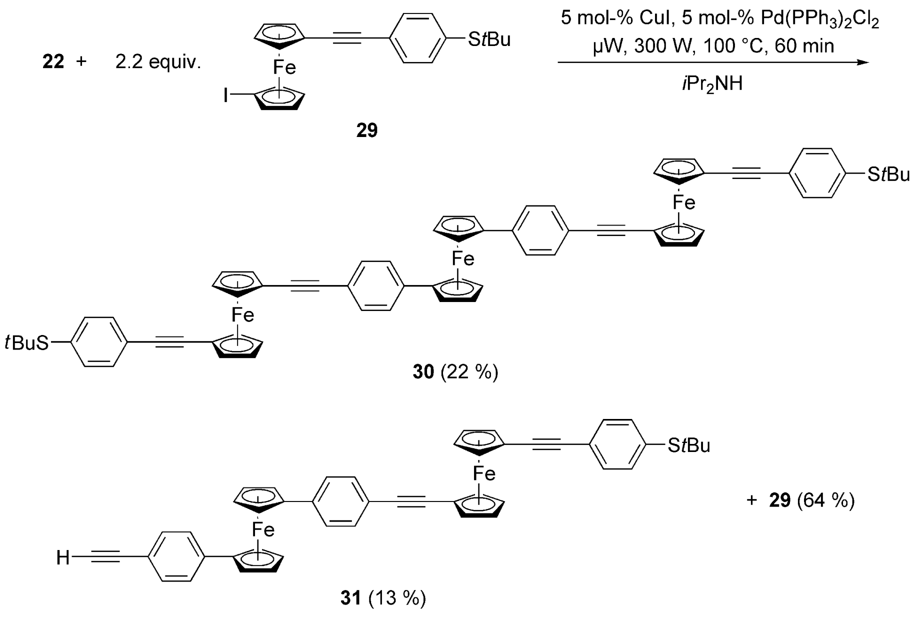
Although **25** is a building block that allows the attachment of an alligator clip and a 1,4-phenylene unit, there are other building blocks that lead to a more significant extension of a molecular wire. We recently reported on the synthesis of ferrocene-based molecular wires with two ferrocene hinges by Sonogashira coupling of **29** with diynes such as 1,4-diethynylbenzene.[10] In contrast to 1,4-diethynylbenzene and related terminal diynes, compounds **22**–**24** provide an additional ferrocene unit, thereby facilitating the synthesis of molecular wires with three ferrocene hinges. To test



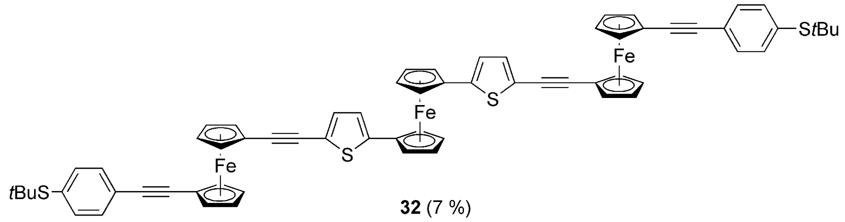
Scheme 8. Sonogashira dialkynylation reactions of **22**–**24** with **25**.

this attractive possibility, **22** and **24** were treated with **29** under Sonogashira coupling conditions. The reaction of **22** afforded double-coupling product **30** in 22% yield along with the mono-coupling product **31**, which was obtained in 13% yield (Scheme 9). In addition, 64% of unconsumed starting material was recovered. The double-coupling product **30** is the first molecular wire of the OPE type with three ferrocene hinges incorporated. Its molecular length based on standard bond lengths is estimated to around 4 nm in its most extended conformation. The mono-coupling product **31** is not only the side-product of an incomplete reaction but a valuable building block in its own right that may serve for the synthesis of unsymmetrical ferrocene-based molecular wires. Compounds **30** and **31** were characterized spectroscopically. Diagnostic features are the alkyne absorptions in the IR spectra, the correct number and integrated ratio of the cyclopentadienyl proton signals in the ^{1}H NMR spectra as well as the correct numbers and multiplicities of ^{13}C NMR signals, and a correct elemental analysis of **30**.

In a similar way, thiophene-derived dialkyne **24** was treated with **29** to afford double-coupling product **32** in 7% yield along with 74% of unconsumed starting material (Scheme 10).



Scheme 9. Synthesis of **30**, the first ferrocene-based OPE containing three ferrocene units.



32 (7 %)

Scheme 10. Double-coupling product **32**.

To learn about the redox behavior of the new ferrocene derivatives prepared in this work, some of them were investigated by cyclic voltammetry. The data obtained are collected in Table 1. For comparison purposes the data for **5** and **6** are also included.

Table 1. Cyclovoltammetry of the new ferrocene derivatives.[a]

	c [10^{-3} mol/L]	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{½}$ [V]
5[b]	0.5	0.381	0.149	0.232	0.265
6[b]	0.5	0.711	0.495	0.216	0.603
14	2	0.158	–0.004	0.162	0.077
15[a]	2	0.212	0.032	0.180	0.122
22	2	0.217	0.055	0.162	0.136
24	2	0.198	0.042	0.156	0.120
26	2	0.129	0.000	0.129	0.065
27	2	0.021	–0.120	0.141	–0.050
28	2	0.141	0.002	0.138	0.072
30	1	0.096	–0.026	0.122	0.035
		0.307	0.115	0.192	0.211
32	0.5	0.186	0.057	0.129	0.121
		0.378	0.219	0.159	0.298

[a] Potentials measured relative to FcH/FcH$^+$, 293 K, c_{TBAPF6} = 0.1 mol/L, v = 100 mV/s, solvent CH_2Cl_2, $TBAPF_6$ = tetrabutylammonium hexafluorophosphate. [b] Data taken from ref.[10].

All the cyclovoltammograms show quasi-reversible oxidation/reduction waves, which have been assigned to the redox processes of the ferrocene moieties. All the oxidation reactions take place at positive potentials relative to ferrocene/ferrocinium, which is in accord with an electron-withdrawing effect of the various aryl substituents. Comparison of the data of **26** with that of **27** reflects the higher electron density in **27**, which is due to the presence of methoxy groups. Remarkably, replacing the 1,4-phenylene in **26** by 2,5-thiophenylene moieties in **28** gives a slightly higher oxidation potential for **28**, which indicates that the presence of the 2,5-thiophenylene units causes the ferrocene to be less easily oxidized than in the presence of 1,4-phenylene groups. This cannot easily be explained on the basis of electron densities because thiophene is regarded as electron-rich compared with benzene. Therefore other reasons such as differences in conformation with respect to the coplanarity of the cyclopentadienyl and substituting π systems or polarity have to be considered. The cyclovoltammograms of **30** and **32**, the first molecular wires with three ferrocene hinges, are shown as representative examples in Figure 2. In both cases two quasi-reversible redox processes are observed. As in the case of thiophene-containing **28**, the oxidation of the thiophene-containing wire **32** requires a higher potential than that of the corresponding phenylene-derived system **30**. Based on a comparison of the oxidation potentials of the two processes in **30** and **32** with those observed for **26**, **28**, and **5**, the first oxidation step in **30** and **32** has to be assigned to the oxidation of the aryl- or hetaryl-substituted central ferrocene moiety and the second oxidation step to the alkynyl-substituted outer ferrocene moieties. Solubility problems with **32** made it necessary to perform the measurement of this compound at a lower concentration (see Table 1), which makes it difficult to compare

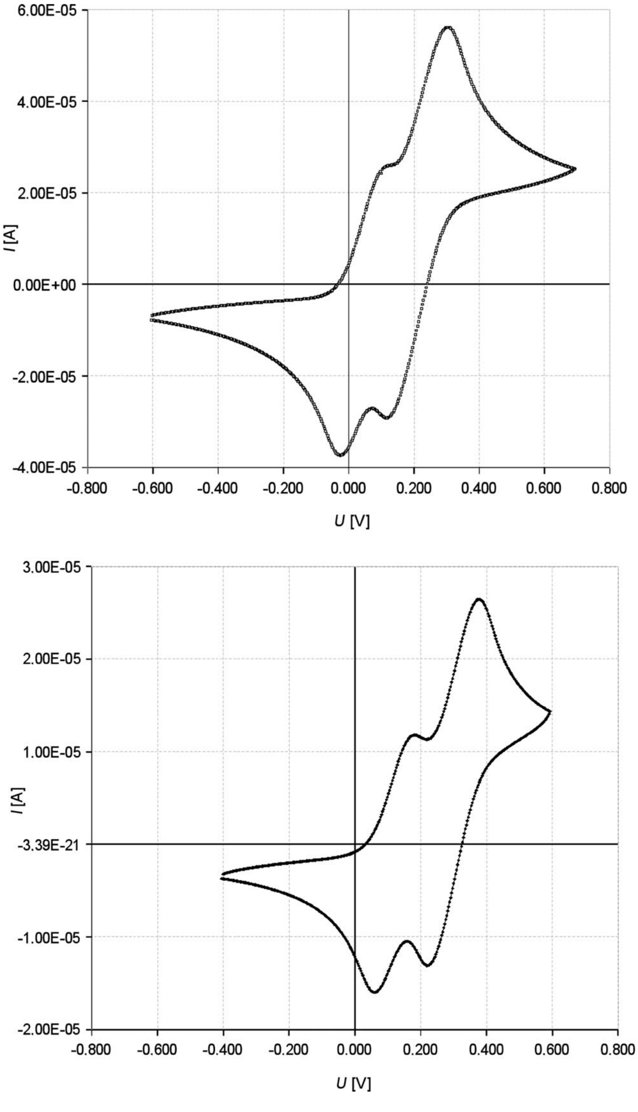


Figure 2. Cyclovoltammograms of **30** (top) and **32** (bottom). Potential vs. FcH/FcH$^+$. For further details see Table 1.

the currents of the two measurements. However, the significantly higher currents are in accord with the presence of two ferrocene moieties available for the second oxidation step.

Conclusions

We have prepared a number of 1,1′-diarylated ferrocenes by Negishi coupling reactions under microwave irradiation. These compounds serve as building blocks for ferrocene-based molecular wires of the OPE type. The X-ray structure analysis of 1,1′-bis(thiophenylene) derivative **24** shows an eclipsed conformation with almost coplanar ferrocene and thiophene rings in the solid state. Sonogashira coupling reactions have allowed the first syntheses of ferrocene-based molecular wires with three ferrocene hinges incorporated. A number of the compounds prepared have been characterized by cyclic voltammetry.

Experimental Section

General: All reactions were performed using the Schlenk technique with nitrogen or argon as the inert gas. All glassware was heated at <0.1 mbar with a heat gun prior to use to remove any oxygen or water. Tetrahydrofuran (THF), diethyl ether, and toluene were dried with sodium/potassium alloy/benzophenone and distilled. Pentane, petroleum ether, and dichloromethane were dried with CaH_2 and distilled. Starting materials were either commercially acquired or were prepared according to published procedures. Ferrocene was a donation from Innospec Deutschland GmbH.

^1H and ^{13}C NMR spectra were obtained with Bruker AVS 200 (^1H: 200 MHz) and AVS 400 (^1H: 400 MHz; ^{13}C: 100.6 MHz) instruments. Chemical shifts (δ) are referenced to $\delta_{TMS} = 0$ ppm or to residual solvent signals. Signal multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Primary, secondary, tertiary, and quaternary carbon signals were identified as such by the APT and DEPT techniques. In some cases signal assignments were based on 2D NMR spectra (HMQC, HMBC). IR spectra were obtained with Perkin–Elmer FT-IR 580 and 1170 instruments. Signal characteristics are abbreviated as s (strong), m (medium), and w (weak). Mass spectra were obtained with a Micromass LC-TOF-MS instrument with a lock-spray source and direct injection with an ionization potential of 70 eV. Analytical TLC was performed with Merck 60F-254 silica gel thin-layer plates. Column chromatography was performed with J. T. Baker silica gel (40 µm) as the stationary phase using the flash chromatography method.[38] Elemental analyses were obtained with a Heraeus CHN Rapid instrument. Reactions under microwave irradiation (µW) were performed with a CEM Discover™ Labmate reactor under nitrogen ("open vessel") using the ChemDriver software. The temperature was monitored by means of an IR sensor. Some reactions were performed using the PowerMax™ method. Cyclic voltammetry (CV) measurements were performed under argon with a Gamry Instruments Reference 600 potentiostat/galvanostat/ZRA with 0.1 mol/L tetrabutylammonium hexafluorophosphate electrolyte in acetonitrile or dichloromethane at 25 °C. Ag/Ag^+ ($AgNO_3$) was used as the reference electrode in acetonitrile with 0.01 mol/L $AgNO_3$ and 0.1 mol/L tetrabutylammonium hexafluorophosphate. Platinum was used for the working and counter electrodes. The system was calibrated with ferrocene/ferrocinium and the values measured are referenced to FcH/FcH^+.

General Procedure for the Negishi Coupling Under Microwave Irradiation: At –78 °C 1.6 M butyllithium (2.1 equiv.) in hexane was added to 1,1′-dibromoferrocene (**8**; 1.0 equiv.)[28,29] in THF in a Schlenk flask. Within 30 min at –78 °C an orange suspension of 1,1′-dilithioferrocene formed. After warming to 0 °C anhydrous $ZnCl_2$ (2.1 equiv.) was added as a solid or dissolved in THF. The reaction mixture was stirred at 0 °C for 90 min. A suspension of the palladium catalyst [prepared in situ from 5.0 mol-% of $[Pd(PPh_3)_2Cl_2]$ and 10 mol-% of DIBAL-H (20 wt.-% in toluene)] in THF and then the aryl iodide (2.1 equiv.) were added in one portion. The mixture was stirred in a microwave reactor (100 W, 70 °C, 60 min, 10 min ramp time). After cooling to 25 °C dilute aqueous sodium hydroxide was added and after phase separation the mixture was extracted three times with an equivalent volume of dichloromethane. The organic layers were collected and dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was dissolved in a small amount of dichloromethane and a double volume of silica gel was added. After solvent removal under reduced pressure the adsorbed product was isolated by column chromatography.

1,1′-Bis(4-bromophenyl)ferrocene (10):[39] Compound **10** was prepared by following the general procedure using **8** (1000 mg, 2.9 mmol) in THF (25 mL), 1.6 M butyllithium in hexane (4.0 mL, 6.4 mmol), $ZnCl_2$ (867 mg, 6.4 mmol), $[Pd(PPh_3)_2Cl_2]$ (98 mg, 5 mol-%), DIBAL-H (0.26 mL, 10 mol-%, 20 wt.-% in toluene), and 1-bromo-4-iodobenzene (1800 mg, 6.4 mmol). Purification by column chromatography (30 × 3 cm, petroleum ether/dichloromethane, 4:1) yielded 897 mg (1.8 mmol, 63 %) of **10** as orange crystals, identified by ^1H and ^{13}C NMR comparison.[25]

1,1′-Bis(4-fluorophenyl)ferrocene (11):[25] Compound **11** was prepared by following the general procedure using **8** (923 mg, 2.7 mmol) in THF (25 mL), 1.6 M butyllithium in hexane (3.3 mL, 5.3 mmol), $ZnCl_2$ (728 mg, 5.3 mmol), $[Pd(PPh_3)_2Cl_2]$ (94 mg, 5 mol-%), DIBAL-H (0.25 mL, 10 mol-%, 20 wt.-% in toluene), and 1-fluoro-4-iodobenzene (1190 mg, 6.4 mmol). Purification by column chromatography (30 × 3 cm, petroleum ether/dichloromethane, 10:1) yielded 610 mg (1.6 mmol, 61 %) of **11** as orange crystals, identified by ^1H and ^{13}C NMR comparison.[25]

1,1′-Bis(4-methoxyphenyl)ferrocene (12):[27] Compound **12** was prepared by following the general procedure using **8** (868 mg, 2.5 mmol) in THF (25 mL), 1.6 M butyllithium in hexane (3.1 mL, 5.0 mmol), $ZnCl_2$ (684 mg, 5.0 mmol), $[Pd(PPh_3)_2Cl_2]$ (88 mg, 5 mol-%), DIBAL-H (0.23 mL, 10 mol-%, 20 wt.-% in toluene), and 4-iodo-1-methoxybenzene (1170 mg, 5.0 mmol). Purification by column chromatography (30 × 3 cm, petroleum ether/ethyl acetate, 10:1) yielded 695 mg (1.8 mmol, 70 %) of **12** as orange-red crystals, identified by ^1H and ^{13}C NMR comparison.[40]

1,1′-Bis[4-(ethoxycarbonyl)phenyl]ferrocene (13):[41] Compound **13** was prepared by following the general procedure using **8** (716 mg, 2.1 mmol) in THF (25 mL), 1.6 M butyllithium in hexane (2.6 mL, 4.2 mmol), $ZnCl_2$ (566 mg, 4.2 mmol), $[Pd(PPh_3)_2Cl_2]$ (73 mg, 5 mol-%), DIBAL-H (0.19 mL, 10 mol-%, 20 wt.-% in toluene), and ethyl 4-iodobenzoate (1150 mg, 5.0 mmol). Purification by column chromatography (deactivated SiO_2, 30 × 3 cm, petroleum ether/ethyl acetate, 10:1) yielded 792 mg (1.6 mmol, 79 %) of **13** as orange-red crystals, identified by ^1H and ^{13}C NMR comparison.[41]

1,1′-Bis[4-(*tert*-butylsulfanyl)phenyl]ferrocene (14): Compound was prepared by following the general procedure using **8** (516 mg, 1.5 mmol) in THF (25 mL), 1.6 M butyllithium in hexane (2.0 mL, 3.2 mmol), $ZnCl_2$ (429 mg, 3.2 mmol), $[Pd(PPh_3)_2Cl_2]$ (55 mg, 5 mol-%), DIBAL-H (0.20 mL, 10 mol-%, 20 wt.-% in toluene), and *tert*-butyl(4-iodophenyl)sulfane (920 mg, 3.2 mmol). Purification by column chromatography (SiO_2, 30 × 3 cm, petroleum ether/dichloromethane, 5:1) yielded 407 mg (0.8 mmol, 53%) of **14** as an orange solid (m.p. 158 °C). IR: ṽ = 3065 (w), 2968 (m), 2919 (m), 2858 (m), 1597 (m), 1513 (m), 1449 (m), 1362 (m), 1279 (m), 1261 (m), 1167 (m), 1104 (m), 1028 (m), 1015 (m), 881 (m), 831 (s), 815 (s), 733 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 18 H, CH_3), 4.25 [m, 4 H, 3(3′)-H], 4.44 [m, 4 H, 2(2′)-H], 7.25 [d, ^3J = 8.2 Hz, 4 H, SCCHC*H*], 7.39 [d, ^3J = 8.2 Hz, 4 H, SCCH] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 31.1 (CH_3), 46.0 (*C*CH$_3$), 68.5 (C-2 or C-3), 71.0 (C-3 or C-2), 85.2 (C-1), 126.0 (SCCH*C*H), 130.0 (S*C*CH), 137.5 (SC*C*H), 139.2 (SCCHCH*C*C) ppm. HRMS: calcd. for $C_{30}H_{34}FeS_2$ 514.1451; found 514.1454. $C_{30}H_{34}FeS_2$ (514.57): calcd. C 70.02, H 6.66; found C 69.84, H 6.74.

1,1′-Bis[4-(trimethylsilylethynyl)phenyl]ferrocene (15). Method A: In a Schlenk flask $Cu(OAc)_2{\cdot}H_2O$ (18 mg, 10 mol-%) was added to **10** (502 mg, 1.0 mmol) in triethylamine (30 mL). The mixture was degassed by carrying out three freeze–pump–thaw cycles. Trimethylsilylethyne (250 mg, 2.5 mmol) and $[Pd(PPh_3)_2Cl_2]$ (36 mg, 5 mol-%) were added and the mixture was stirred at reflux for 18 h. After cooling to 25 °C, a satd. aqueous NH_4Cl solution (30 mL) was added. The aqueous layer was extracted with 30 mL portions of dichloromethane until the organic layer remained colorless. The collected organic layers were dried with $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (SiO_2, 30 × 3 cm, petroleum ether/dichloromethane, 5:1) gave 469 mg (0.9 mmol, 89%) of **15** as a red solid (m.p. 152 °C).

Method B: Compound **15** was prepared by following the general procedure using **8** (754 mg, 2.2 mmol) in THF (20 mL), 1.6 M butyllithium in hexane (2.9 mL, 4.6 mmol), $ZnCl_2$ (624 mg, 4.6 mmol), $[Pd(PPh_3)_2Cl_2]$ (77 mg, 5 mol-%), DIBAL-H (0.20 mL, 10 mol-%, 20 wt.-% in toluene), and 1-(4-iodophenyl)-2-trimethylsilyl)ethyne (1170 mg, 4.8 mmol). Purification by column chromatography (SiO_2, 30 × 3 cm, petroleum ether/dichloromethane, 5:1 → 2:1) have two fractions. I: 153 mg (0.4 mmol, 9%) of [4-(trimethylsilylethynyl)phenyl]ferrocene;[42] II: 731 mg (1.4 mmol, 63%) of **15**. IR: ṽ = 3102 (Ar), 2957 (CH_3), 2154 (C≡C), 1593 (Ar), 814 (1,4-disubst. Ar) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 18 H, CH_3), 4.23 [m, 4 H, 3(3′)-H], 4.40 [m, 4 H, 2(2′)-H], 7.23 (d, ^3J = 8.2 Hz, 4 H, SiC≡CCCHC*H*), 7.35 [d, ^3J = 8.5 Hz, 4 H, SiC≡CCCH] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 0.2 (CH_3), 68.5 (C-2), 71.1 (C-3), 85.0 (C-1), 94.3 (SiC≡*C*C), 105.6 (Si*C*≡CC), 120.5 (SiC≡C*C*), 125.7 (SiC≡CCCH*C*H), 132.1 (SiC≡CC*C*H), 139.3 (SiC≡CCCHCH*C*C) ppm. HRMS: calcd. for $C_{32}H_{34}FeSi_2$ 530.1548; found 530.1544. $C_{32}H_{34}FeSi_2$ (530.63): calcd. C 72.43, H 6.46; found C 72.34, H 6.65.

In some experiments a partial hydrodesilylation of **15** was observed resulting in small amounts of 1-[4-(trimethylsilylethynyl)phenyl]-1′-(4-ethynylphenyl)ferrocene, which was isolated as a red solid (m.p. 138 °C). IR: ṽ = 3304 (m, Ar), 2955 (m), 2158 (m, C≡C), 1606 (w), 1522 (m), 1453 (m), 1245 (m), 1033 (m), 832 (s), 758 (s), 698 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 9 H, CH_3), 3.12 (s, 1 H, CC≡CH), 4.23–4.25 (m, 4 H, 3(3′)-H), 4.42–4.46 (m, 4 H, 2(2′)-H), 7.17–7.21 (m, 4 H, CH_{Ar}), 7.30–7.34 (m, 4 H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 0.2 (CH_3), 68.2 (C-2 or C-2′), 68.3 (C-2′ or C-2), 70.99 (C-3 or C-3′), 71.0 (C-3′ or C-3), 77.2 (CC≡*C*H), 84.2 (C*C*≡CH), 85.1 (C-1 or C-1′), 85.2 (C-1′ or C-1), 94.3 (SiC≡*C*C), 105.6 (Si*C*≡CC), 119.4 (SiC≡C*C* or HC≡C*C*), 120.5 (HC≡C*C* or SiC≡C*C*), 125.6 (SiC≡CCCH*C*H or HC≡CCCH*C*H), 125.7 (HC≡CCCH*C*H or SiC≡CCCH*C*H), 132.1 (SiC≡CC*C*HCH or HCCC*C*HCH), 132.3 (HCCC*C*HCH or SiC≡CC*C*HCH), 138.8 (SiC≡CCCHCH*C*C or HCCCCHCH*C*C), 139.2 (HCCCCHCH*C*C or SiC≡CCCHCH*C*C) ppm. HRMS: calcd. for $C_{29}H_{26}FeSi$ 458.1153; found 458.1151. $C_{29}H_{26}FeSi$ (458.45): calcd. C 75.98, H 5.72; found C 76.28, H 5.86.

1,1′-Bis[2,5-dimethoxy-4-(trimethylsilylethynyl)phenyl]ferrocene (16) and [2,5-Dimethoxy-4-(trimethylsilylethynyl)]ferrocene (17): Compound **16** was prepared by following the general procedure using **8** (380 mg, 1.5 mmol) in THF (20 mL), 1.6 M butyllithium in hexane (1.5 mL, 2.4 mmol), $ZnCl_2$ (331 mg, 2.4 mmol), $[Pd(PPh_3)_2Cl_2]$ (39 mg, 5 mol-%), DIBAL-H (0.10 mL, 10 mol-%, 20 wt.-% in toluene), and [(4-iodo-2,5-dimethoxyphenyl)ethynyl]trimethylsilane (876 mg, 2.4 mmol). Purification by column chromatography (SiO_2, 30 × 3 cm, petroleum ether/dichloromethane, 1:2) yielded two fractions. I: 97 mg (0.2 mmol, 21%) of **17** as a red solid (m.p. 125 °C); II: 144 mg (0.22 mmol, 20%) of **16** as a red solid (m.p. 115 °C).

16: IR: ṽ = 2957 (m, Ar), 2850 (w, OCH_3), 2150 (s, C≡C), 1511 (s), 1464 (s), 1217 (s), 1040 (s), 839 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 18 H, $SiCH_3$), 3.77 (s, 6 H, SiC≡CCCOCH$_3$), 3.84 (s, 6 H, SiC≡CCCHCOC*H*$_3$), 4.20 [m, 4 H, 3(3′)-H], 4.58 [m, 4 H, 2(2′)-H], 6.90 [s, 2 H, SiC≡CCC(OCH$_3$)C*H*], 6.91 [s, 2 H, SiC≡CCCH] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 0.3 ($SiCH_3$), 56.0 (SiC≡CCCO*C*H$_3$), 56.8 (SiC≡CCCHCO*C*H$_3$), 70.8 (C-2, C-3), 82.7 (C-1), 98.6 (SiC≡*C*), 101.8 (Si*C*≡C), 110.1 (SiC≡C*C*), 112.5 [SiC≡CCC(OCH$_3$)*C*H], 116.5 (SiC≡CC*C*H), 129.7 [SiC≡CCC(OCH$_3$)CH*C*], 150.6 (SiC≡CCCH*C*OCH$_3$), 154.7 (SiC≡CC*C*OCH$_3$) ppm. MS (ESI): calcd. for $C_{36}H_{42}FeO_4Si_2$ + H 651.2049; found 651.2037.

17: IR: ṽ = 2958 (m, Ar), 2847 (w, OCH_3), 2153 (s, C≡C), 1510 (s), 1464 (m), 1213 (s), 1032 (s), 837 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 9 H, $SiCH_3$), 3.86 (s, 3 H, SiC≡CCCOCH$_3$), 3.90 (s, 3 H, SiC≡CCCHCOC*H*$_3$), 4.03 (s, 5 H, Cp), 4.31 (m, 2 H, 3-H), 4.78 (m, 2 H, 2-H), 6.94 [s, 1 H, SiC≡CCC(OCH$_3$)C*H*], 7.03 (s, 1 H, SiC≡CCCH) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 0.3 ($SiCH_3$), 56.1 (SiC≡CCCO*C*H$_3$), 56.8 (SiC≡CCCHCO*C*H$_3$), 69.0 (C-2 or C-3), 69.2 (C-3 or C-2), 69.7 (C_{Cp}), 82.0 (C-1), 98.6 (SiC≡*C*), 101.8 (Si*C*≡C), 110.0 (SiC≡C*C*), 112.5 [SiC≡CCC(OCH$_3$)*C*H], 116.7 (SiC≡CC*C*H), 130.2 [SiC≡CCC(OCH$_3$)CH*C*C], 150.6 [SiC≡CCCH*C*(OCH$_3$)], 154.8 (SiC≡CC*C*OCH$_3$) ppm. HRMS: calcd. for $C_{23}H_{26}FeO_2Si$ 418.1051; found 418.1054. $C_{23}H_{26}FeO_2Si$ (418.38): calcd. C 66.03, H 6.26; found C 65.43, H 6.38.

1-Bromo-1′-(4-nitrophenyl)ferrocene (18): Compound **18** was prepared by following the general procedure using **8** (1210 mg, 3.5 mmol) in THF (20 mL), 1.6 M butyllithium in hexane (4.6 mL, 7.0 mmol), $ZnCl_2$ (957 mg, 7.0 mmol), $[Pd(PPh_3)_2Cl_2]$ (82 mg, 3 mol-%), DIBAL-H (0.23 mL, 10 mol-%, 20 wt.-% in toluene), and 1-iodo-4-nitrobenzene (1750 mg, 7.0 mmol) after microwave irradiation stirring for 12 h at 25 °C. Purification by column chromatography (deactivated SiO_2, 30 × 3 cm, petroleum ether/dichloromethane, 5:1, then petroleum ether/ethyl acetate, 5:1) yielded 343 mg (0.9 mmol, 26%) of **18** as dark-red crystals (m.p. 119 °C). IR: ṽ = 3095 (w, Ar), 3081 (w), 2919 (w), 2865 (w), 1592 (s), 1499 (s), 1412 (m), 1320 (s), 1287 (s), 1111 (m), 1083 (m), 1012 (m), 891 (m), 869 (m), 845 (s), 816 (s), 755 (m), 691 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.02 (m, 4 H, Cp), 4.23 (m, 4 H, Cp), 4.54 (m, 4 H, Cp), 4.74 (m, 4 H, Cp), 7.59 [d, ^3J = 8.9 Hz, 4 H, NCHC*H*], 8.17 [d, ^3J = 8.9 Hz, 4 H, NCCH] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC, $CDCl_3$): δ = 69.0 (C_{Cp}), 69.7 (C_{Cp}), 72.2 (C_{Cp}), 73.0 (C_{Cp}), 78.5 (C-1 or C-1′), 83.7 (C-1′ or C-

1), 124.0 (NC*C*H), 126.5 (NCCH*C*H), 146.0 (NCCHCH*C*C), 146.6 (NC) ppm. MS: *m*/*z* (%) = 387 (97) [M$^+$ (^{81}Br)]$^+$, 386 (29), 385 (100) [M (^{79}Br)]$^+$, 341 (44) [M – NO$_2$]$^+$, 307 (50) [M – Br]$^+$, 261 (26) [M – Br – NO$_2$]$^+$, 139 (77) [CpPh]$^+$, 56 (27) [Fe]$^+$. $C_{16}H_{12}BrFeNO_2$ (390.05): calcd. C 49.78, H 3.13, N 3.63; found C 50.39, H 3.33, N 3.63.

1,1′-Bis(5-bromo-2-thienyl)ferrocene (19): Compound **19** was prepared by following the general procedure using **8** (1100 mg, 3.2 mmol) in THF (20 mL), 1.6 M butyllithium in hexane (4.0 mL, 6.4 mmol), $ZnCl_2$ (868 mg, 6.4 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (112 mg, 5 mol-%), DIBAL-H (0.3 mL, 10 mol-%, 20 wt.-% in toluene), and 5-bromo-2-iodothiophene (1840 mg, 6.4 mmol).[43] Purification by column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/ethyl acetate, 10:1) yielded 111 mg (0.4 mmol, 11%) of **19** as wine-red crystals (m.p. 145 °C). IR: $\tilde{\nu}$ = 3068 (w), 3054 (w), 1544 (w), 1469 (m), 1414 (m), 1251 (m), 1222 (w), 1051, (m), 1030 (m), 956 (s), 851 (m), 814 (s), 797 (s), 784 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.23 [m, 4 H, 3(3′)-H], 4.40 [m, 4 H, 2(2′)-H], 6.59 (d, $^3J_{5,6}$ = 3.8 Hz, 2 H, BrCCHC*H*), 6.90 (d, $^3J_{6,5}$ = 3.8 Hz, 2 H, BrCCH) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 68.2 (C-2 or C-3), 70.6 (C-3 or C-2), 81.1 (C-1), 109.2 (CBr), 122.9 (BrCCH*C*H), 130.3 (BrC*C*H), 143.1 (BrCCHCH*C*C) ppm. HRMS: calcd. for $C_{18}H_{12}S_2FeBr_2$ 505.8097; found 505.8094. $C_{18}H_{12}S_2FeBr_2$ (508.07): calcd. C 42.55, H 2.38; found C 43.06, H 2.53.

1,1′-Bis[5-(trimethylsilylethynyl)-2-thienyl]ferrocene (20) and [5-(Trimethylsilylethynyl)-2-thienyl]ferrocene (21): Compounds **20** and **21** were prepared by following the general procedure using **8** (770 mg, 2.2 mmol) in THF (20 mL), 1.6 M butyllithium in hexane (3.1 mL, 4.9 mmol), $ZnCl_2$ (668 mg, 4.9 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (77 mg, 5 mol-%), DIBAL-H (0.20 mL, 10 mol-%, 20 wt.-% in toluene), and 2-iodo-5-(trimethylsilylethynyl)thiophene (1500 mg, 4.9 mmol).[44] Purification by column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 5:1 to 2:1) yielded two fractions. I: 61 mg (0.2 mmol, 8%) of **21** as a dark-red oil; II: 506 mg (0.9 mmol, 42%) of **20** as a red solid (m.p. 123 °C).

20: IR: $\tilde{\nu}$ = 3097 (w), 2957 (w), 2898 (w), 2137 (s, C≡C), 1249 (m), 1163 (m), 838 (s), 814, 801 (m), 758 (m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.27 (s, 18 H, CH$_3$), 4.23 [m, 4 H, 3(3′)-H], 4.42 [m, 4 H, 2(2′)-H], 6.69 (d, ^3J = 3.7 Hz, 2 H, SiC≡CCCHC*H*), 7.02 (d, ^3J = 3.7 Hz, 2 H, SiC≡CCCH) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 0.1 (CH$_3$), 68.9 (C-2 or C-3), 71.3 (C-3 or C-2), 80.6 (C-1), 98.2 (SiC≡*C*), 99.0 (Si*C*≡C), 120.5 (SiC≡C*C*), 122.4 (SiC≡CCCH*C*H), 133.5 (SiC≡CC*C*H), 144.3 (SiC≡CCS*C*) ppm. HRMS: calcd. for $C_{28}H_{30}FeS_2Si_2$ 542.0677; found 542.0671. $C_{28}H_{30}FeS_2Si_2$ (542.68): calcd. C 61.97, H 5.57; found C 62.05, H 5.76.

21: IR: $\tilde{\nu}$ = 3298 (w), 2957 (m), 2140 (s, C≡C), 2093 (w), 1542 (w), 1424 (w), 1249 (s), 1164 (m), 1024 (w), 1001 (w), 839 (s), 758 (s), 730 (m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.26 (s, 9 H, CH$_3$), 4.09 (s, 5 H, Cp), 4.30 (m, 2 H, 3-H), 4.56 (m, 2 H, 2-H), 6.83 (d, ^3J = 3.7 Hz, 1 H, SiCCCCHC*H*), 7.05 (d, ^3J = 3.7 Hz, 1 H, SiCCCCH) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 0.1 (CH$_3$), 67.2 (C-2 or C-3), 69.2 (C-3 or C-2), 70.3 (Cp), 79.1 (C-1), 98.3 (SiC*C*), 98.9 (Si*C*C), 120.3 (SiCC*C*), 121.9 (SiCCCCH*C*H), 133.4 (SiCCC*C*H), 145.9 (SiCCCS*C*) ppm. HRMS: calcd. for $C_{19}H_{20}FeSSi$ 364.0404; found 364.0402. $C_{19}H_{20}FeSSi$ (364.36): calcd. C 62.63, H 5.53; found C 62.23, H 5.36.

1,1′-Bis(4-ethynylphenyl)ferrocene (22)

Method A: At 25 °C, 1 M tetrabutylammonium fluoride in THF (4.8 mL, 4.8 mmol) was added to **15** (1260 mg, 2.4 mmol) in dichloromethane (20 mL). The mixture was stirred at 25 °C for 30 min. Then water (30 mL) was added. The aqueous layer was extracted with 30 mL portions of dichloromethane until these remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 5:1) gave 919 mg (2.4 mmol, 100%) of **22** as an orange-red solid (m.p. 137 °C).

Method B: At 25 °C, K$_2$CO$_3$ (521 mg, 3.8 mmol) was added to **15** (200 mg, 0.4 mmol) in dichloromethane/methanol (5:1, 20 mL). After stirring for 12 h at 25 °C, dichloromethane (30 mL) was added. The mixture was washed with satd. aqueous NaCl (30 mL) and the aqueous layer was extracted with 30 mL portions of dichloromethane until these remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 10 × 3 cm, petroleum ether/dichloromethane, 5:1) gave 147 mg (0.4 mmol, 100%) of **22**.

IR: $\tilde{\nu}$ = 3285 (s, C≡CH), 3096 (w), 2922 (w), 2101 (w, C≡C), 1606 (m), 1520 (m), 825 (s), 809 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.13 (s, 2 H, C≡CH), 4.25 [m, 4 H, 3(3′)-H], 4.45 [m, 4 H, 2(2′)-H], 7.19 [d, ^3J = 8.5 Hz, 4 H, HC≡CCCHC*H*], 7.32 [d, ^3J = 8.5 Hz, 4 H, HC≡CCC*H*] ppm. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.64 (s, 2 H, C≡CH), 4.28 [m, 4 H, 3(3′)-H], 4.62 [m, 4 H, 2(2′)-H], 7.29–7.32 [m, 8 H, HC≡CCC*H*C*H*] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 68.0 (C-2), 70.9 (C-3), 77.1 (C≡*C*H), 84.0 (*C*≡CH), 84.9 (C-1), 119.3 (HC≡C*C*), 125.5 (HC≡CCCH*C*H), 132.1 (HC≡CC*C*H), 138.9 (HC≡CCCHCH*C*C) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, [D$_6$]acetone): δ = 68.7 (C-2), 71.8 (C-3), 78.9 (*C*≡CH), 84.6 (C≡*C*H), 85.7 (C-1), 120.3 (HC≡C*C*), 126.6 (HC≡CCH*C*H), 132.7 (HC≡C*C*H), 139.9 (HC≡CCCHCH*C*C) ppm. HRMS: calcd. for $C_{26}H_{18}Fe$ 386.0758; found 386.0760. $C_{26}H_{18}Fe$ (386.27): calcd. C 80.85, H 4.70; found C 80.40, H 4.86.

1,1′-Bis(4-ethynyl-2,5-dimethoxyphenyl)ferrocene (23): At 25 °C, K$_2$CO$_3$ (425 mg, 3.1 mmol) was added to **17** (200 mg, 0.3 mmol) in dichloromethane/methanol (5:1, 20 mL). After stirring for 12 h at 25 °C, dichloromethane (30 mL) was added. The mixture was washed with satd. aqueous NaCl (20 mL) and the aqueous layer was extracted with 20 mL portions of dichloromethane until these remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 10 × 3 cm, petroleum ether/dichloromethane, 1:2) gave 155 mg of **23** (0.3 mmol, 100%) as a red solid (m.p. 92 °C). IR: $\tilde{\nu}$ = 3275 (w, C≡CH), 2922 (m), 2850 (m), 2327 (w, C≡C), 2099 (w), 1604 (m), 1509 (m), 1464 (m), 1387 (m), 1282 (m), 1213 (s), 1034 (s), 909 (w), 861 (m), 817 (m), 782 (m), 728 (m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.35 (s, 2 H, C≡CH), 3.74 (s, 6 H, HC≡CCCHCOC*H*$_3$), 3.84 (s, 6 H, HC≡CCCOC*H*$_3$), 4.25 [m, 4 H, 3(3′)-H], 4.64 [m, 4 H, 2(2′)-H], 6.86 [m, 4 H, arom. CH] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 55.9 (HC≡CCO*C*H$_3$), 56.5 (HC≡CCCHCO*C*H$_3$), 70.5 (C-2 or C-3), 70.7 (C-3 or C-2), 80.6 (HC≡*C*), 81.1 (H*C*≡C), 82.8 (C-1), 108.8 (HC≡C*C*), 111.9 [HC≡CCC(OCH$_3$)*C*H], 116.5 (HC≡CC*C*H), 129.3 [HC≡CCC(OCH$_3$)CH*C*C], 150.5 (HC≡CCCH*C*OCH$_3$), 154.7 (HC≡CC*C*OCH$_3$) ppm. HRMS: calcd. for $C_{30}H_{26}FeO_4$ 506.1180; found 506.1179.

1,1′-Bis(5-ethynyl-2-thienyl)ferrocene (24): At 25 °C, 1 M tetrabutylammonium fluoride (1.8 mL, 1.8 mmol) in THF was added to **20** (452 mg, 0.8 mmol) in dichloromethane (20 mL). The mixture was stirred at 25 °C for 30 min. Then water (25 mL) was added. The aqueous layer was extracted with 25 mL portions of dichloromethane until these remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 5:1) gave 305 mg (0.8 mmol, 92%) of **24** as a red solid (m.p. 138 °C). IR: ṽ = 3285 (s, C≡CH), 2095 (w, C≡C) 1422 (m), 817 (s), 795 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.39 (s, 2 H, C≡CH), 4.25 [m, 4 H, 3(3′)-H], 4.45 [m, 4 H, 2(2′)-H], 6.68 (d, ^3J = 3.8 Hz, 2 H, HC≡CCCHC*H*), 7.04 (d, ^3J = 3.7 Hz, 2 H, HC≡CCC*H*) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 68.8 (C-2 or C-3), 71.1 (C-3 or C-2), 77.7 (C≡*C*H), 80.6 (C-1), 81.4 (HC≡*C*), 119.3 (HC≡C*C*), 122.3 (HC≡CCCH*C*H), 133.9 (HC≡CC*C*H), 144.1 (HC≡CS*C*) ppm. HRMS: calcd. for $C_{22}H_{14}FeS_2$ 397.9886; found 397.9884. $C_{22}H_{14}FeS_2$ (399.32): calcd. C 66.34, H 3.54; found C 65.98, H 3.69.

Crystal Structure Analysis of 24:[30] Crystals were obtained as orange-red needles by slow solvent evaporation from dichloromethane/pentane at 25 °C. Empirical formula $C_{22}H_{14}FeS_2$, molecular weight 397.99 g/mol, crystal system orthorhombic, space group $Pna2_1$, a = 16.993(6), b = 17.521(7), c = 5.9704(2) Å, α = 90, β = 90, γ = 90°, V = 1777.7(11) Å^3, Z = 1, $d_{\text{calcd.}}$ = 1.488 Mg/m^3, F(000) = 816, μ = 1.084 mm^{-1}, crystal size 0.3 × 0.2 × 0.1 mm, Stoe IPDS area detector diffractometer, T = 297 K, λ(Mo-K_α) = 0.71073 Å, $\theta_{\min}$ = 2.32, $\theta_{\max}$ = 26.17°, $-20 \le h \le 20$, $-21 \le k \le 21$, $-7 \le l \le 7$, no absorption correction, no extinction correction, reflections collected 3512, unique 2467 [R(int) = 0.0316], completeness to θ = 26.17, 98.9%. Refinement method: full-matrix least-squares on F^2. Data 3004, restraints 1, parameters 226, goodness-of-fit on F^2 0.904, final R indices [$I > 2\sigma(I)$] $R1$ = 0.0316, wR_2 = 0.0527, R indices (all data) $R1$ = 0.0541, wR_2 = 0.0551, largest diff. peak and hole 0.358 and –0.173 e A^{-3}.

1,1′-Bis{4-[4-(*tert*-butylsulfanyl)phenylethynyl]phenyl}ferrocene (26): [Ph(PPh$_3$)$_2$Cl$_2$] (9 mg, 5 mol-%) was added to a solution of **22** (100 mg, 0.3 mmol), **25** (167 mg, 0.6 mmol),[10] and CuI (3 mg, 5 mol-%) in diisopropylamine (20 mL). After stirring at 60 °C for 18 h and cooling to 25 °C, satd. aqueous NH$_4$Cl (20 mL) was added and the aqueous layer was extracted with 20 mL portions of dichloromethane until the organic layer remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was evaporated under reduced pressure. Column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 2:1) gave 86 mg (0.1 mmol, 47%) of **26** as an orange solid (m.p. 229–240 °C). IR: ṽ = 2959 (m), 2920 (w), 2212 (w, C≡C), 1603, (w), 1587 (w), 1524 (m), 1482 (w), 1454 (w), 1363 (m), 1260 (m), 1083 (m), 1015 (m), 832 (s), 819 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.31 (s, 18 H, CH$_3$), 4.28 [m, 4 H, 3(3′)-H], 4.49 [m, 4 H, 2(2′)-H], 7.21–7.23 [m, 4 H, SC$_6$H$_4$CCCCHC*H*], 7.35–7.37 [m, 4 H, SC$_6$H$_4$CCCC*H*], 7.46–7.48 [m, 8 H, SCC*H*C*H*] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 31.2 (CH$_3$), 46.6 (*C*CH$_3$), 68.2 (C-2 or C-3), 71.0 (C-3 or C-2), 85.3 (SC$_6$H$_4$*C*≡CC), 89.1 (SC$_6$H$_4$C≡*C*C), 91.5 (C-1), 120.4 (SC$_6$H$_4$C≡C*C*), 124.0 (SCCHCH*C*C≡CC), 125.8 (SC$_6$H$_4$C≡CCCH*C*H), 131.6 (SC$_6$H$_4$C≡CCCH*C*H), 131.8 (SC$_6$H$_4$C≡CC*C*H), 133.2 (S*C*CH), 137.4 (SC*C*H), 138.6 (SC$_6$H$_4$C≡CCCHCH*C*) ppm. MS (ESI): calcd. for $C_{46}H_{42}FeS_2$ 714.2077; found 714.2068. $C_{46}H_{42}FeS_2$ (714.80): calcd. C 77.29, H 5.92; found C 76.40, H 6.44.

1,1′-Bis{4-[4-(*tert*-butylsulfanyl)phenylethynyl]-2,5-dimethoxyphenyl}ferrocene (27): [Pd(PPh$_3$)$_2$Cl$_2$] (14 mg, 5 mol-%) was added to a degassed solution of **23** (184 mg, 0.4 mmol), **25** (319 mg, 1.1 mmol),[10] and CuI (4 mg, 5 mol-%) in diisopropylamine (10 mL). The mixture was heated by microwave irradiation at 300 W and 85 °C for 60 min (+ 15 min ramp time). After cooling to 25 °C, satd. aqueous NH$_4$Cl (25 mL) was added and the aqueous layer was extracted with 25 mL portions of dichloromethane until these remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 1:2) afforded 137 mg (0.2 mmol, 45%) of **27** as an orange solid (m.p. 198 °C). IR: ṽ = 2958 (m), 2922 (m), 2852 (m), 2210 (w, C≡C), 1515 (s), 1469 (s), 1400 (m), 1215 (s), 1162 (m), 1044 (s), 856 (m), 837 (m), 807 (m), 766 (m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.30 (s, 18 H, CH$_3$), 3.78 (s, 6 H, SC$_6$H$_4$C≡CCCOC*H*$_3$), 3.87 (s, 6 H, SC$_6$H$_4$C≡CCCHCOC*H*$_3$), 4.27 [m, 4 H, 3(3′)-H], 4.68 [m, 4 H, 2(2′)-H], 6.89 [s, 2 H, SC$_6$H$_4$C≡CCC(OCH$_3$)C*H*], 6.91 (s, 2 H, SC$_6$H$_4$C≡CCC*H*), 7.45–7.49 (m, 8 H, SCC*H*C*H*) ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 31.1 (CH$_3$), 46.6 (S*C*CH$_3$), 55.9 (SC$_6$H$_4$C≡CCCO*C*H$_3$), 56.6 (SC$_6$H$_4$C≡CCCHCO*C*H$_3$), 70.5 (C-2 or C-3), 70.7 (C-3 or C-2), 83.0 (SC$_6$H$_4$*C*≡C), 88.0 (SC$_6$H$_4$C≡*C*), 92.9 (C-1), 109.9 (SC$_6$H$_4$C≡C*C*), 112.2 [SC$_6$H$_4$C≡CCC(OCH$_3$)-*C*H], 115.9 (SC$_6$H$_4$C≡CC*C*H), 124.2 [SCCHCH*C*C≡C], 129.0 [SC$_6$H$_4$C≡CCCHC(OCH$_3$)*C*C], 131.6 (SC*C*H), 133.0 (S*C*CH), 137.3 (SCCH*C*H), 150.7 (SC$_6$H$_4$C≡CCCH*C*OCH$_3$), 154.2 (SC$_6$H$_4$C≡CC*C*OCH$_3$) ppm. MS (ESI): calcd. for $C_{50}H_{50}FeO_4S_2$ + Na$^+$ 857.2398; found 857.2395. $C_{50}H_{50}FeO_4S_2$ (834.90): calcd. C 71.93, H 6.04; found C 72.05, H 6.71.

1,1′-Bis{5-[4-(*tert*-butylsulfanyl)phenylethynyl]-2-thienyl}ferrocene (28): [Pd(PPh$_3$)$_2$Cl$_2$] (6 mg, 5 mol-%) and CuI (2 mg, 5 mol-%) were added to a degassed solution of **24** (62 mg, 0.2 mmol) and **25** (137 mg, 0.5 mmol)[10] in diisopropylamine (10 mL) and acetonitrile (10 mL). The mixture was stirred at 25 °C for 3 d and then satd. aqueous NH$_4$Cl (20 mL) was added and the aqueous layer was extracted with 25 mL portions of dichloromethane until these remained colorless. The collected organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 2:1) afforded 65 mg (0.1 mmol, 58%) of **28** as an orange solid (m.p. 168 °C). IR: ṽ = 3095 (w), 2958 (m), 2921 (m), 2896 (m), 2857 (m), 2199 (m, C≡C), 1470 (m), 1427 (m), 1363 (m), 1217 (m), 1166 (m), 1039 (m), 973 (m), 830 (s), 817 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.31 (s, 18 H, CH$_3$), 4.28 [m, 4 H, 3(3′)-H], 4.49 [m, 4 H, 2(2′)-H], 6.74 (d, ^3J = 3.8 Hz, 2 H, C≡CCSCC*H*), 7.06 (d, ^3J = 3.8 Hz, 2 H, C≡CCSCCHC*H*), 7.46 [AA′BB′, 8 H, H$_3$CSCC*H*C*H*] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, CDCl$_3$): δ = 31.2 (CH$_3$), 46.7 (*C*CH$_3$), 68.7 (C-2 or C-3), 71.0 (C-3 or C-2), 80.9 (SC$_6$H$_4$*C*≡C), 85.0 (C-1), 92.9 (SC$_6$H$_4$C≡*C*), 120.4 (SC$_6$H$_4$C≡C*C*S), 122.7 (C≡CCSC*C*H), 123.7 (H$_3$CCSCCHCH*C*), 131.3 (H$_3$CCSCCH*C*H), 133.0 (C≡CCSCCH*C*H), 133.3 (H$_3$CCS*C*), 137.4 (H$_3$CCSC*C*H), 144.2 (C≡CCS*C*C) ppm. MS (ESI): calcd. for $C_{42}H_{38}FeS_4$ 726.1206; found 726.1212. $C_{42}H_{38}FeS_4$ (726.86): calcd. C 69.40, H 5.27; found C 69.29, H 5.68.

1,1′-Bis(4-{1′-[4-(*tert*-butylsulfanyl)phenylethynyl]ferrocen-1-ylethynyl}phenyl)ferrocene (30) and 1-(4-{1′-[4-(*tert*-Butylsulfanyl)phenylethynyl]ferrocen-1-ylethynyl}phenyl)-1′-(4-ethynylphenyl)ferrocene (31): CuI (4 mg, 5 mol-%) and [Pd(PPh$_3$)$_2$Cl$_2$] (13 mg, 5 mol-%) were added to a degassed solution of **22** (140 mg, 0.4 mmol) and **29** (399 mg, 0.8 mmol)[10] in diisopropylamine (20 mL). The mixture was heated by microwave irradiation (300 W) at 100 °C for 60 min (+ 15 min ramp time). After cooling to 25 °C, dichloromethane (20 mL) and satd. aqueous NH$_4$Cl (20 mL) was added. The aqueous layer was extracted with portions of 20 mL dichloromethane until these remained colorless. The combined organic layers were dried with MgSO$_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO$_2$, 30 × 3 cm, petroleum ether/dichloromethane, 1:1) gave three fractions. I: 90 mg

(0.1 mmol, 22%) of **30** as an orange solid (m.p. 199 °C); II: 37 mg (0.05 mmol, 13%) of **31** as an orange solid (m.p. 127 °C); III: 205 mg (0.5 mmol, 64%) of unreacted **29**.

30: IR: ṽ = 2958 (w), 2920 (w), 2208 (w, C≡C), 1604 (w), 1530 (m), 1454 (w), 1417 (w), 1364 (m), 1281 (w), 1163 (w), 1088 (w), 1027 (m), 1016 (m), 919 (m), 832 (s), 820 (s), 731 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 18 H, CH_3), 4.24 (m, 4 H, Cp), 4.32–4.36 (m, 8 H, Cp), 4.46 (m, 4 H, Cp), 4.56–4.57 (m, 8 H, Cp), 7.21 [d, ^3J = 8.5 Hz, 4 H, Cp-CC*H*CHCC≡C], 7.31 [d, ^3J = 8.2 Hz, 4 H, Cp-CCHC*H*CC≡C], 7.41 [AA′BB′, 8 H, $H_3CCSC_6H_4$C≡C] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 31.1 (CH_3), 46.5 (H_3C*C*), 66.7 (C_{Fc}C≡C), 67.4 (C_{Fc}C≡C), 68.2 (Cp), 71.2 (Cp), 71.4 (Cp), 73.1 (Cp), 73.2 (Cp), 85.3 (C-1), 86.2 (C≡), 87.1 (C≡), 87.4 (C≡), 89.3 (C≡), 121.2 (CpC≡C*C*CHCHCCp), 124.4 (SCCHCH*C*C≡C), 125.8 (CpCCH), 131.5 (CpCCHC*H*), 131.6 (SCCH), 132.6 (H_3CCS*C*), 137.3 (SCCHC*H*), 138.4 (CpCCHC*H*) ppm. MS (APCI): calcd. for $C_{70}H_{58}Fe_3S_2$ 1130.2028; found 1130.2037. $C_{70}H_{58}Fe_3S_2$ (1130.87): calcd. C 74.35, H 5.17; found C 74.49, H 5.53.

31: IR: ṽ = 2957 (w), 2154 (m, C≡C), 1605 (w), 1523 (m), 1415 (w), 1246 (s), 1106 (w), 1004 (w), 835 (s), 758 (s), 731 (s), 666 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9 H, CH_3), 3.13 (s, 1 H, C≡CH), 4.24–4.26 (m, 4 H, Cp), 4.34–4.35 (m, 2 H, Cp), 4.37–4.38 (m, 2 H, Cp), 4.46–4.47 (m, 4 H, Cp), 4.57–4.59 (m, 4 H, Cp), 7.17 (d, 2 H, H_{Ar}), 7.22 (d, 2 H, H_{Ar}), 7.28 (d, 2 H, H_{Ar}), 7.35 (d, 2 H, H_{Ar}), 7.44 [dd, 4 H, SCC*H*C*H*] ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.1 (CH_3), 46.5 (*C*CH_3), 66.7 (C_{Cp}C≡C), 67.5 (C_{Cp}C≡C), 68.1 (Cp), 68.2 (Cp), 71.0 (Cp), 71.1 (Cp), 71.2 (Cp), 71.4 (Cp), 73.1 (Cp), 73.2 (Cp), 77.3 (HC≡$CC_6H_4C_{Cp}$) 84.2 (*H*C≡C), 85.0 (C-1), 85.4 (C≡), 86.2 (C≡), 87.1 (C≡), 87.4 (C≡), 89.3 (C≡), 119.4 (HC≡C*C*), 121.2 (CpCCHCH*C*), 124.4 (SCCHCHC), 125.70 (HC≡CCC*H* or CpCCHC*H*), 125.73 (HC≡CCC*H* or CpCCHC*H*), 131.48 (HC≡CCCHC*H* or CpC*C*H), 131.54 (SCCHC*H*), 132.3 (HC≡CCCHC*H* or CpC*C*H), 132.6 (S*C*CH), 137.3 (SC*C*H), 137.9 (Cp*C*CH), 139.2 (Cp*C*CH) ppm.

1,1′-Bis(5-{1′-[4-(*tert*-butylsulfanyl)phenylethynyl]ferrocen-1-ylethynyl}-2-thienyl)ferrocene (32): CuI (2 mg, 5 mol-%) and [$Pd(PPh_3)_2Cl_2$] (6 mg, 5 mol-%) were added to a degassed solution of **24** (73 mg, 0.2 mmol) and **29** (202 mg, 0.4 mmol)[10] in diisopropylamine (20 mL). The mixture was heated by microwave irradiation (300 W) at 100 °C for 60 min (+ 15 min ramp time). After cooling to 25 °C, dichloromethane (20 mL) and satd. aqueous NH_4Cl (20 mL) were added. The aqueous layer was extracted with portions of 20 mL dichloromethane until these remained colorless. The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2, 30 × 3 cm, petroleum ether/dichloromethane, 1:1) yielded 15 mg (0.01 mmol, 7%) of **32** as an orange solid (m.p. 186 °C). IR: ṽ = 3072 (w), 2957 (m), 2921 (m), 2852 (m), 2213 (w, C≡C), 1727 (w), 1542 (w), 1468 (m), 1421 (m), 1364 (m), 1165 (m), 1029 (m), 1018 (m), 973 (m), 911 (m), 862 (m), 839 (s), 816 (s), 801 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 18 H, CH_3), 4.24 (m, 4 H, Cp), 4.33–4.36 (m, 8 H, Cp), 4.44 (m, 4 H, Cp), 4.55–4.58 (m, 8 H, Cp), 6.70 (d, ^3J = 3.8 Hz, 2 H, C≡CCSCC*H*), 6.93 (d, ^3J = 3.8 Hz, 2 H, C≡CCSCCHC*H*), 7.44 [AA′BB′, 8 H, C_6H_4] ppm. ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$): δ = 31.1 (CH_3), 46.5 (*C*CH_3), 66.8 (C≡CC_{Cp}), 67.0 (C≡CC_{Cp}), 68.7 (Cp), 71.3 (Cp), 71.3 (Cp), 71.4 (Cp), 73.1 (C-2 or C-3), 73.2 (C-3 or C-2), 80.4 (C≡), 80.8 (C≡), 86.3 (C-1), 89.2 (C≡), 91.5 (C≡), 121.3 (C≡C*C*S), 122.7 (C≡CCSC*C*H), 124.4 (H_3CCSCCHCH*C*), 131.5 (H_3CCCHC*H*), 132.1 (C≡CCSCCHC*H*), 132.6 (H_3CCS*C*), 137.3 (H_3CCSC*C*H), 143.3 (CpC*S*) ppm. MS (ESI): calcd. for $C_{66}H_{54}Fe_3S_4$ 1142.1157; found 1142.1124.

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