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Functionalised biferrocene systems towards molecular electronics

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Abstract: Biferrocene systems offer a motif that incorporates multiple redox-active centres, enabling redox control, high levels of stability and near perfect conductance levels, and thus is an ideal participant within future molecular electronic systems. However, the incorporation of biferrocene can be restricted by current synthetic routes. Herein, we discuss a new methodology for the synthesis and incorporation of biferrocenyl motifs within extended conjugated systems. We have synthesised a family of compounds featuring biferrocenyl-ethynyl units with various pendant heteroaromatic linkages. The new compounds are probed using cyclic voltammetry, UV/vis/NIR spectroelectrochemistry and X-ray crystallography to gain further understanding of their structural and electronic properties.

Introduction

Since the discovery of ferrocene in the 1950's, its beauty, stability and electronic character has kept chemists captivated.^[1] At the beginning of the 21st century, ferrocene was incorporated into molecular wires, and has since exhibited excellent conduction levels, much higher than the corresponding organic systems.^[2] This is in addition to ferrocene's ability to serve as an redox-active unit, where it can switch between a highly conductive oxidized state and a less conductive neutral state.^[3] The incorporation of multiple ferrocene units within a system allows attainment of a greater variety of oxidation states and the added effects of communication between the centres. Multiple ferrocene units have been incorporated into molecular wires with bridging units between them, displaying how communication between the systems can be tuned.^[4] Other reports have utilized the biferrocene motif within wire-like structures, and shown their suitability as SAMs (self-assembly monolayers) as well as bridging units between other metal centres.^[5] These studies indicate that the biferrocene motif can be a better conductor than a single ferrocene unit e.g. allowing electron transfer between terminating metals through 1,1'-bis(ethynyl)biferrocene systems.^[6] The versatility of uses, the excellent electronic characteristics and the variation in synthetic strategies that can be achieved, make the biferrocene motif an attractive unit within

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the field of molecular electronics.^[7]

Ferrocenes and biferrocenes may also exhibit spin related control, known as spintronic effects.^[5a, 8] Systems have previously been proposed containing both ferrocene and cobaltocene.^[9] To recognise any of these effects we need to investigate these molecules further on an electronic level. The surface binding group has a large influence on the overall conductivity of the system.^[10] For example, the type and strength of binding are key factors. Groups such as thiols demonstrate a very strong level of bonding, while in comparison the thioether unit is weaker. [11] It has been shown that the strength of the bond is not always the main factor in surface ligation^[12] e.g. although the thiol bond is strong, the pyridyl unit has a much higher probability of junction formation due to bond orientation and too strong bonds can cause ruptures on the gold surface.^[13] To add to the actual binding, the conductance mechanisms must also be addressed in order to pair the binding group with the molecule and surface.^[10] All these factors therefore need investigating further within molecular systems.

We herein present and discuss a new synthetic route to a range of functionalised biferrocene containing molecular wire precursors, alongside electrochemical, spectroelectrochemical and X-ray crystallographic characterization. These new compounds contain different surface binding groups and orientations, allowing for the study of the effect of the binding group within these molecular systems.

Results and Discussion

Synthesis

The traditional synthesis of biferrocene-containing molecules passes through the use of the 1,1"'-diiodobiferrocene motif.^[14] The synthesis of 1,1"'-diiodobiferrocene is unpredictable with yields varying between (7%-28%).^[15] We here propose the use of an Ullmann-like coupling to form the motif within the required molecules. Previously Ullmann coupling of halo-ferrocenes used activated copper bronze, high temperatures and long reaction times.^[16] However, it has been shown how the use of copper(I)thiophene-2-carboxylate (CuTC) as a metal mediator can form biferrocene in excellent yields (81%)^[15b] Utilizing this method has allowed the synthesis of a series of biferrocene molecules, shown in Scheme 1.



Scheme 1. Synthetic route to linear biferrocene molecules

Our method was first applied to the synthesis of the phenyl terminated system **2.1**, previously synthesised through the 1,1"-iodobiferrocene route.^[14] This was to identify if the alkynyl group altered the synthesis in comparison to the simple biferrocene system and if this method was an improvement on the previous synthetic route.

1.1 was synthesised using a palladium-catalysed Sonogashira cross-coupling reaction. The product was achieved in high yields over the di-substituted ferrocene by-product by using a large excess of 1,1'-diiodoferrocene to alkyne (5:1). The product was then easily separated from the excess 1,1'-diiodoferrocene through column chromatography to give a yield of 74%. Product **2.1** was formed by a homo-coupling of **1.1**, using CuTC in *N*-methyl-2-pyrrolidone (NMP). The NMP was extracted from the product using *n*-hexane/brine. The pure product was gained through column chromatography to give a yield of 69%, thus confirming that the substitution of the iodoferrocene motif had little effect on the efficiency of the reaction. This also shows a much greater overall yield to product formation than the previously reported method.^[14]

2.1 is a synthetically interesting product but does not allow the study of 'through-molecules' conductance using scanning tunnelling microscopy (STM) on a gold substrate, as it does not contain gold binding groups. Thus our synthetic procedure was extended to the pyridine-terminated system, as pyridine is a well-studied binding group and shows high conductivity.^[17] The synthesis of **1.2** was achieved with acceptable yields of 52%, through the same method previously discussed, thus enabling the Ullman-like coupling to proceed to the formation of **2.2**. The product was only isolated in low yields (15%), as there were a large amount of impurities found within the reaction mixture. This is thought to be due to pyridine-catalysed side reactions.

As an alternative to the pyridine system, incorporation of a thioether functionality was developed. The thioether group is also a suitable binding group for these molecules, as demonstrated by SAMs and single molecule studies.^[18] The *ortho*-substituted molecule **2.3** was synthesized and purified in the same way as **2.1**. The methodology worked well for

thioether-containing molecules as the final yield was 53% and the reaction formed far less by-products than that of **2.2**. In order to investigate how the substitution pattern of the binding groups could affect the surface-binding properties of the compounds, the *meta*- and *para*-substituted analogues were also synthesized **(2.3** and **2.4)**. These were isolated in yields of 71% and 42%, respectively.

Electrochemistry. The electrochemical properties of the materials synthesised were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 , using 0.1 M [(ⁿBu)₄N]PF₆ as the supporting electrolyte. Relevant data are summarized in Table 1.

Table 1. Electrochemical data for cyclic voltammetry experiments with 0.1M $[(^nBu)_4N]PF_6/CH_2Cl_2^a$

Cmp.	E _{1/2} ¹	ΔE^1	<i>I</i> _{pa} / <i>I</i> _{pc} ¹	$E_{1/2}^{2}$	ΔE^2	$I_{\rm pa}/{I_{pc}}^2$	$\Delta E^1 E^2$
Fc ₂	-0.06	0.070	1.00	0.324	0.067	0.85	0.384
2.1 ^b	0.041	0.061	1.01	0.397	0.061	0.84	0.355
2.3	0.048	0.069	1.01	0.401	0.063	0.99	0.353
2.4	0.051	0.062	1.04	0.402	0.060	0.91	0.351
2.5	0.033	0.062	1.04	0.382	0.064	0.93	0.349
[a]Conditions: scan rate 0.02 V s ⁻¹ ; Working electrode: Glassy Carbon; Counter and reference electrode: Pt wire; All potentials reported in V							

Counter and reference electrode: Pt wire; All potentials reported in V relative to an internal $[Cp_2Fe]/[Cp_2Fe]^*$ reference and corrected for iR_s . Measured against an internal $[Cp^*_2Fe]/[Cp^*_2Fe]^*$ reference (-0.495 V vs $[Cp_2Fe]/[Cp_2Fe]^*$ in our system) [b] scan rate 0.03 V s⁻¹

CV experiments show two discrete reversible redox events for all biferrocene molecules (Figure 1). The electrochemical experiments are reported for all compounds in a $[(^{n}Bu)_{4}N]PF_{6}/DCM$ solution, apart from the pyridine molecule **2.2**, as this shows instability within this electrolyte. This instability is discussed further in the supporting information (Figures S11-15).

In a fully reversible system, ΔE should be independent of scan rate. These results show a strong agreement with this when corrected for solution resistance effects (using values of R_s estimated from AC impedance spectroscopy).^[19] In a reversible system, a value of $\Delta E \approx 59$ mV at room temperature, is expected for a one electron exchange. These systems all show values that are close to this for both redox events at low scan rates. This indicates chemical and electrochemical ideality of these redox events and where deviation does occur it could be due to ion pairing effects. If $i_{pc}/i_{pa} \approx 1$ and $\Delta E \approx 59$ mV at room temperature, high reversibility of a system is indicated. Redox events for all molecules show both these characteristics (see Table 1). When $i_p \propto v_s^{1/2}$ the redox event is a pure diffusion process. These are displayed in the supporting information (Figures S16 and S17).

We attribute all redox features to the Fe^{2+}/Fe^{3+} couples.^[20] The first redox event is the Fe^{2+}/Fe^{3+} of one of the ferrocene centres

at a lower potential, followed by the second redox event at a higher potential. The display of two redox events is due to two separate oxidations. This sequence of events can be thought of as displayed in equation **1**. The mixed-valent state, that occurs when one metal centre is oxidised, can be described by the *Robin-Day classification*, which discusses the degree of delocalisation within a system.^[21]

$$[Fe_1^{2+} Fe_2^{2+}]^0 \rightleftharpoons [Fe_1^{3+} Fe_2^{2+}]^1 \rightleftharpoons [Fe_1^{3+} Fe_2^{3+}]^2$$
(1)

The splitting between the two redox events allows for the calculation of the comproportionation constant $K_{\rm com}$, using equation **2**. The value of $K_{\rm com}$ provides the first indication as to whether the mixed-valent system can be classified as charge localised, slightly delocalised or completely delocalised (Class I, II or III respectively).^[22]

$$K_{\rm com} = 10^{(\rm F} \cdot \Delta E^{\circ} / 2.303 \cdot RT)$$
⁽²⁾

For our systems, $\Delta E^{\circ} \approx 350 \text{ mV}$ which gives a $K_{\rm com} \approx 10^5 \cdot 10^6$. This agrees well with findings on other biferrocenium cations, which have been assigned as class II/III borderline systems i.e. in between totally and partially delocalized states on the basis of Mössbauer studies.^[23] This also shows that the addition of external attachments has little effect on the delocalization within conjugated ferrocene and metal centres.^[24]



Figure 1. Solution electrochemistry for **2.5**. Cyclic (top) and differential pulse (bottom) voltammograms recorded in 0.1M [(^{n}Bu)₄N]PF₆/CH₂Cl₂ (*E* vs. [Cp₂Fe]⁺, corrected for *i*R_s)

The equilibrium potentials $E_{1/2}$ are an indication of the energy required for oxidising each metal centre. When molecules (2.1, 2.3-2.5) are compared, all exhibit higher $E_{1/2}$ values than the biferrocene molecule **Fc**₂. This is expected due to the electron withdrawing effect of the ethynyl motif on the ferrocene units.^[25]

The addition of the electron withdrawing thioether group seems to have little effect on the $E_{1/2}$, in comparison to **2.1** or through the different orientations.

The pyridine system (2.2) does not produce stable electrochemical data in (ⁿBu)₄N]PF_{6.} However, it was possible to gain results with a NaBArF electrolyte. A similar discrepancy between ferrocene systems and electrolytes was also reported by Inkpen *et al.* although this was due to the higher oxidations and not connected to a pyridine motif.^[15b]

Molecule **2.2** shows two redox events, as seen and discussed for the previous systems. The voltammogram is shown in the supporting information (Figure S15) and the values are displayed in Table 2. Even in the NaBArF electrolyte a small shoulder can be seen at higher potential for molecule **2.2**, which is expected to be due to some instability of the system. Due to variation in electrolyte these values are not comparable to the previously discussed measurements. We therefore compare them to system **2.3** in the same conditions.

The values $i_{pc}/i_{pa} \approx 1$ suggest that **2.2** is also a reversible system within these conditions. In comparison to **2.3** (and presumably all other systems), **2.2** has a higher equilibrium potential ($E_{1/2}$). This is due to the electron withdrawing properties of the pyridine motif having an electronic effect on the biferrocene moiety. $\Delta E^1 E^2$ and ΔE values for **2.2** and **2.3** are both larger than those reported for the (ⁿBu)₄N]PF₆ experiments due to the reduction in ion-pairing effects of the NaBArF electrolyte. The relative values of the molecules are very similar, thus we suggest that structural differences have no effect on the values.

Table 2. Electrochemical data for cyclic voltammetry experiments with ~0.01M NaBArF/CH_2Cl_2 $\,$

Cmp.	$E_{1/2}^{1}$	ΔE^1	<i>I</i> _{pa} / <i>I_{pc}¹</i>	$E_{1/2}^{2}$	ΔE^2	$I_{\rm pa}/I_{pc}^2$	$\Delta E^1 E^2$
2.2	0.179	0.078	0.92	0.754	0.078	0.88	0.575
2.3	0.115	0.076	0.96	0.713	0.089	0.97	0.598

Conditions: scan rate 0.02 V s⁻¹; Working electrode: Glassy Carbon; Counter and reference electrode: Pt wire; All potentials reported in V relative to an internal $[Cp_2Fe]/[Cp_2Fe]^+$ reference and corrected for iR_s . Measured against an internal $[Cp_2Fe]/[Cp_2Fe]^+$ reference (-0.495 V vs $[Cp_2Fe]/[Cp_2Fe]^+$ in our system)

UV/vis/NIR Spectroelectrochemistry

Spectroscopic changes in the UV/vis/near infrared (NIR) region of complexes **2.1** and **2.3** to **2.5** in their neutral, mono- and dioxidized states have been probed by spectroelectrochemistry in an OTTLE (optical transparent thin layer electrolysis) cell constructed according to the design of Hartl et al.^[26] The results of these experiments are depicted in Figure 2 and Figures S18-20 of the Supporting Information (SI), while electronic absorption data and extinction coefficients are summarized in Table **3.** As

an aid to the interpretation of experimental spectra, we performed (TD-)DFT calculations. In the phenyl and the pyridyl substituted congeners 2.1 and 2.2, the HOMO is equally distributed over both ferrocenyl subunits of the biferrocenyl core with only minor contributions from the ethynyl linkers and even smaller ones from the aryl substituents. In contrast, the HOMO and HOMO-1 of biferrocenes 2.3, 2.4 and 2.5 with ortho-, metaor para-positioned SMe substituents are almost degenerate and are strongly biased to one arylethynyl ferrocene subunit with sizable contributions from the arylethynyl pendant, in particular for the para and the ortho isomers, where the SMe donor is in better conjugation with the phenylethynyl group (Figure S21). Taken together, the HOMO and HOMO-1 represent in- and outof-phase combinations with respect to the arylethynyl pendants. As expected, the HOMO of the pyridylethynyl-substituted biferrocene 2.2 is energetically stabilized by 0.055 eV with respect to its phenylethynyl analogue 2.1, signalling that the oxidation potentials should be modestly higher, which is also reflected in the redox potentials.



Figure 2. UV/vis/NIR spectroelectrochemistry of 2.1 in 1,2dichloroethane/NBu₄PF₆ (0.1 M); blue = neutral state; red = monooxidised state; green = dioxidised state.

Table 3. UV/vis/NIR spectroscopic properties of all complexes in their accessible oxidation states. $^{\rm [a]}$

No	λ_{max} / nm (ϵ / 10 ³ M ⁻¹ cm ⁻¹)
2.1	456 (1.3)
2.1*	420 (5.3), 677 (2.6), 1998 (1.1)
2.1 ²⁺	374 (11.1), 459 (7.3), 659 (1.2) 872 (1.8)
2.3	323 (sh), 455 (1.6)
2.3+	398 (sh) 670 (1.86), 2018 (0.9)
2.3 ²⁺	389 (sh), 501 (4.7), 670 (1.0), 924 (1.1)
2.4	305 (sh), 455 (1.7)
2.4*	431 (sh), 676 (2.2), 2051 (1.1)
2.4 ²⁺	381 (sh), 473 (sh), 653 (1.0), 879 (1.5)
2.5	455 (2.2)
2.5 ⁺	442 (sh), 678 (2.4), 884 (1.6), 2057 (0.9)
2.5 ²⁺	380 (sh), 501 (10.0), 702 (1.1), 1016 (2.8)
[a] Data	obtained in 1.2-dicbloroethane/NBU/PE $_{0}$ (0.1 M) at room temperature:

[a] Data obtained in 1,2-dichloroethane/NBu₄PF₆ (0.1 M) at room temperature; sh = transition observed as shoulder.

The highly intense $\pi-\pi^{\star}$ transitions expected in UV/vis spectroscopic measurements fall outside the accessible detection window of the 1,2-dichloroethane/NBu₄PF₆ supporting electrolyte and can only be inferred from the steep rise of absorptivity at wavelengths below 300 nm. Corresponding transitions are, however, predicted by our TD-DFT calculations, e.g. at 303 nm for compound **2.1**. They arise from HOMO-2 to LUMO (52 %) and HOMO-1 to LUMO+1 (33 %) excitations and thus involve considerable biferrocene-to-arylethynyl charge-transfer contributions (see Figure 3).

Upon oxidation to the corresponding mixed-valent radical cation, a band at around 670 nm (see Table 3) grows with only minor differences in terms of position and intensity between the individual complexes. According to our TD-DFT calculations, that band has considerable intervalence charge-transfer (IVCT) character. This is exemplified for complex 2.1⁺, where the corresponding absorption is computed to arise from mixed HOMO-2(α) \rightarrow LUMO(α) (39% contribution), HOMO(α) \rightarrow LUMO(α) (29% contribution) and HOMO- $2(\beta) \rightarrow LUMO(\beta)$ (11% contribution) excitations. As is evident from the MO representations in Figure 3, these transitions arise either from MOs that are delocalized over both arylethynyl ferrocene subunits (HOMO-2(α), HOMO-2(β)) or localised on just one such subunit (HOMO(α)) while LUMO(α) and LUMO(β) are almost completely localized on just one arylethynyl ferrocene site (the other one as (HOMO(α)). Monooxidized complexes (radical cations) 2.1⁺ and 2.3⁺ to 2.5⁺ also feature an electronic transition in the NIR at around 2000 nm. In line with results from cyclic voltammetry, biferrocene 2.2 rapidly decomposed during oxidation inside the OTTLE cell. Complex 2.1 was also studied in the IR/NIR range and here another NIR band at 3010 nm (3320 cm⁻¹) was observed in addition to the higher-energy NIR band at 1960 nm (5106 cm⁻¹) matching the band already observed in the UV/vis/NIR experiment (λ_{max} = 1998 nm, see Table 3). Such bands are typical of mixed-valent biferrocenium radical cations, including the ones derived from biferrocene and diethyl biferrocene as reported by Bally and Tuczek and from macrocyclic oligoferrocene rings.^[15b, 27] For the former biferrocenium radical cations, two NIR bands with similar energy and extinction coefficients were observed and assigned to IVCT

excitations between the symmetric and antisymmetric combinations of the d_x^{2} , ² Fe 3d orbitals (lower energy band) or from the antibonding combination of the d_z^2 Fe 3d orbitals to the symmetric combination of the d_x^{2} , ² orbitals. We propose that the NIR bands of the present biferrocenium radical cations are of similar origin but note that our TD-DFT calculations did not produce any absorption at such low energies.

The IVCT character of the NIR band(s) is also supported by our observation that they are fully bleached on the second oxidation to the corresponding dications. The latter are characterised by rather strong absorptions at around 500 nm, a weaker band at similar energies as the Vis band of the radical cations and a stronger band at ca. 870-1000 nm. Considering the tendency of the MOs to localize either at the biferrocene core or the arylethynyl appendices, some of these bands are likely associated with charge transfer between the core and the periphery.

IVCT bands of biferrocenium cations are usually quite weak despite strong electronic coupling. We therefore studied the solvatochromic behaviour of the NIR bands in 2.1+ as a representative example, using 1,2-dichlorobenzene, CH₂Cl₂, acetone and propylene carbonate as the solvents (note that rapid decomposition of 2.1⁺ was observed in THF and methanol). As shown in Figure S22 and Table S1 of the Supporting Information, there are only very minor changes in peak positions and intensities. Such invariance of IVCT bands with differences in solvent polarity and refractory index are a typical asset of strongly coupled mixed-valent systems of class III or near the class II/III borderline. Results from quantum chemistry are ambiguous, in that they concentrate the spin and charge density on only one ferrocenyl site whereas there is complete delocalization in 2.2⁺ (for fragment analysis and computed spin densities see Figures S23, S24 and Table S2 of the Supporting Information). neutra

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X-ray Crystallography

two C₅ rings twisted by *ca.* 9.8 and 6.7° respectively (the twists in **2.3** and **2.5** are *ca.* 2.1 and 0.4° respectively). The other noticeable difference is the inclination of the terminal aryl ring at one end of the alkynyl unit with respect to the C₅ ring at the other end, and these inclinations correlate with the relative orientations of the alkynyl and Fc–Fc bonds. For **2.3** and **2.5**, where the alkynyl and Fc–Fc bonds are twisted away from each other by *ca.* 70°, the terminal aryl ring is almost orthogonal to the C₅ ring (*ca.* 84° in each case). For **2.2** and **2.4** however, where the alkynyl and Fc–Fc bonds are almost parallel, the terminal aryl rings are inclined by *ca.* 42 and 22° respectively to the C₅ ring, possibly to avoid a close contact with the proximal C₅ ring of the other ferrocenyl unit.

The structures of 2.2, 2.3, 2.4 and 2.5 were determined by single

crystal X-ray diffraction on crystals grown by solvent layering of

n-hexane/DCM. The crystal structures of 2.2, 2.3, 2.4 and 2.5 all

show the molecules to sit across a centre of symmetry at the

middle of the C6-C6A bond that links the two ferrocenyl units

(see Figures 4 to 7 respectively). The most obvious difference

between the four structures lies in the orientation of the alkynyl

bond C(11)-C(12) compared to the Fc-Fc bond C6-C6A. In the

structures of 2.2 and 2.4 these bonds approach parallel, the

C11–C₅(cent)-···C₅(cent)–C(6A) torsion angles being ca. 10.9

and 7.7° respectively, whilst in 2.3 and 2.5 the torsion angles are

ca. 69.9 and 72.3° respectively. In all four structures the

ferrocenyl units adopt eclipsed conformations for the two C5

rings but, associated with the orientations of the alkynyl and Fc-

Fc bonds, in 2.2 and 2.4 there is a significant distortion with the



Figure. 4 The crystal structure of the C_r symmetric complex 2.2.

Figure 3. Calculated molecular orbitals of neutral and radical cationic 2.1 (pbe1pbe/6-31G(d)/PCM level of theory).

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Figure. 5 The crystal structure of the C_r-symmetric complex 2.3.



Figure. 6 The crystal structure of the C_r-symmetric complex **2.4**.



Figure. 7 The crystal structure of the Cr-symmetric complex 2.5.

Conclusions

We have described an improved methodology to create biferrocenecontaining molecules by avoiding the low yielding 1,1"'-diiodobiferrocene motif and utilized low temperature Ullmann-like coupling techniques. This synthetic route displays improved yields and versatility in the products that can be produced. The structures have been probed through crystallography, electrochemistry, spectroelectrochemistry and DFT

calculations. The crystallography showed a difference in ferrocene torsion angle in the crystal structures of the pairs of 2.2, 2.4 and 2.3, 2.5. The electrochemistry data illustrated the expected increase in oxidation potential due to the alkyne substituent. There is no significant effect of substitution of thioether on the redox potential of the biferrocene moiety. The pyridinyl biferrocene showed decomposition when studied in (ⁿBu)₄N]PF₆. However, results were gained using the NaBArF electrolyte. The pyridinyl biferrocene exhibits a higher oxidation potential due to the electronic communication between the pyridyl and the ferrocene centres. The DFT studies have enabled us to investigate the differences between the HOMO of the molecules, where there are clear differences between the distributions in 2.1, 2.2 and the thioether systems 2.3, 2.4 and 2.5. Accompanying TD-DFT calculations provide evidence for intervalence charge-transfer (IVCT) contributions to electronic absorptions observed for mono-oxidised state of the molecules. This new methodology will enable the synthesis of a wider range and more complex ferrocenecontaining molecules, while the molecules that we have synthesized will allow conductance studies to increase the understanding of the binding and interactions within biferrocene-containing wires.

Experimental Section

General: All reactions were performed using standard air sensitive chemistry and Schlenk line techniques, under an atmosphere of nitrogen. No special precautions were taken to exclude air during the work-up. Solvents used in reactions were collected from solvent towers sparged with nitrogen and dried with 3Å molecular sieves, apart from N-methyl-2pyrrolidone (NMP), which was purchased as anhydrous (99.5%) and diisopropylamine (DIPA), which was distilled on to activated 3Å molecular sieves. 1,1'-diiodoferrocene^[15b] and copper(I)thiophene-2-carboxylate^[28] prepared via reported routes. 3-ethynylpyridine, 2were ethynylthioanisole, 3-ethynylthioanisole and 4-ethynylthioanisole were compared through modification of reported routes.^{[29],[30]} All other compounds were purchased from commercial suppliers and used without further purification.

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to the residual solvent peaks of CDCl₃ at 7.26 and 77.16 ppm, respectively. ¹³C{¹H} spectra were fully assigned where possible using 2D correlation spectroscopy. Coupling constants are measured in Hz. Mass spectrometry analyses were conducted by Lisa Haigh of the Mass Spectrometry Service, Imperial College London. Microanalyses were carried out at the Science Centre, London Metropolitan University, by Stephen Boyer using a Thermo Scientific (Carlo Erba) Flash 2000 Organic Elemental Analyser, configured for %CHN. Cyclic voltammograms were recorded under an atmosphere of argon in CH_2CI_2 / 0.1 [NⁿBu₄]PF₆ on a CHI760C potentiostat (CH Instruments, Austin, Texas) or a Gamry reference 600[™] (Gamry Instruments, Warminter, PA, USA) with a glassy carbon disc as working electrode (diameter = 2.5 mm), and Pt-wire as reference and counter electrodes. Analyte solutions were between 0.1-1 mM. Potentials are reported relative to [Cp2Fe]*/[Cp2Fe], measured against internal [Cp*2Fe]*/[Cp*2Fe] references. Density functional theory (DFT) calculations were applied to determine the electronic structures using the GAUSSIAN 09 program package. Geometry optimizations were performed without any symmetry constraints. Electronic transitions were calculated by the time-dependent DFT (TD-DFT) method. Within G09 calculations the quasirelativistic effective core pseudopotentials and the corresponding optimized set of basis functions for Fe were used.^[31] Polarized triple-ζ basis sets (6-311G*, geometry optimization) was employed for structure optimization and polarized double-ζ basis sets 6-31G(d) (TD-DFT) for the molecular orbitals together with the PBE1

functional. $^{\rm [32]}$ The solvent was described by the polarizable conductor calculation model (CPCM) in TD-DFT calculations. $^{\rm [33]}$

Synthesis of 1-iodo,1'-phenylethynylferrocene (1.1): A solution of 1,1'-diiodoferrocene (5.00 g, 11.42 mmol) in DIPA (20 ml) was degassed under N₂ for 10 min. The solution was transferred to a flask containing phenylacetylene (232 mg, 2.28 mmol) and Cul (17 mg, 0.09 mmol). This solution was degassed under N_2 for a further 10 min. Pd(P^tBu₃)₂ (41 mg, 0.17 mmol) was added to the solution against the flow of N2. The reaction mixture was stirred overnight at room temperature. The solvent was removed and the crude product was purified by chromatography on a silica column, eluted with *n*-hexane/DCM ([1:0] \rightarrow [0:1] v/v) to gain the product as an orange powder (691 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (m, 2H), 7.33 (m, 3H), 4.48 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =2, 2H), 4.45 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ = 2, 2H), 4.26 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ = 2, 2H), 4.24 (pseudo-t, ${}^{3}J_{\alpha\beta}$ = 2, 2H). ¹³C NMR (400 MHz, CD₂Cl₂): δ 131.6 (1C, Ar-C-H), 128.4 (2C, Ar-C-H), 129.0 (2C, Ar-C-H), 123.9 (1C, Ar-C-C=C), 87.2 (1C, -C=C-), 87.1 (1C, -C≡C-), 76.5 (2C, Cp-C-H), 74.2 (2C, Cp-C-H), 72.1 (2C, Cp-C-H), 71.1 (2C, Cp-C-H), 67.8 (1C, Cp-C-C), 41.3 (1C, Cp-C-I). MS ES+: m/z 411.9, ([M+H]+ Calc.: 411.94) (Found: C, 52.37; H, 3.19. Calc. for C₁₈H₁₃Fel C, 52.47; H, 3.18.)

Synthesis of 1-iodo,1'-(3-pyridyl)ethynylferrocene (1.2): Method repeated as for **1.1** with 1,1'-diiodoferrocene (5.36 g, 12.26 mmol), DIPA (25 ml), 3-ethynylpyridine (243 mg, 2.35 mmol), Cul (17 mg, 0.09 mmol) and Pd(P¹Bu₃)₂ (41 mg, 0.17 mmol). The pure product was gained as an orange powder (503 mg, 52%). ¹H NMR (400 MHz, CDCl₃): δ 8.76 (s, 1H), 8.54 (m, 1H), 7.78 (m, 1H), 7.26 (m, 1H), 4.49 (pseudo-t, ³J_{α,β} = 1.9, 2H), 4.46 (pseudo-t, ³J_{α,β} = 1.9, 2H), 4.30 (pseudo-t, ³J_{α,β} = 1.9, 2H), 4.46 (pseudo-t, ³J_{α,β} = 1.9, 2H), 4.30 (pseudo-t, ³J_{α,β} = 1.9, 2H), 4.24 (pseudo-t, ³J_{α,β} = 1.9, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 152.3 (1C), 148.3 (1C), 138.4 (1C), 123.1 (1C), 121.2 (1C), 90.9 (1C), 83.8 (1C), 76.6 (2C), 74.3 (2C), 72.3 (2C), 71.0 (2C) 66.9 (1C), 41.4 (1C). MS ES+: m/z 413.9, ([M+H]⁺ Calc.: 413.94) (Found: C, 49.35; H, 2.88; N, 3.43. Calc. for C₁₇H₁₂FeIN C, 49.44; H, 2.93; N, 3.39.)

Synthesis of 1-iodo,1'-(2-thioanisole)ethynylferrocene (1.3): Method repeated as for **1.1** with 1,1'-diiodoferrocene (2.22 g, 5.06 mmol), DIPA (5 ml), 2-ethynylthioanisole (150 mg, 1.01 mmol), Cul (7.5 mg, 0.04 mmol) and Pd(P^IBu₃)₂ (15.5 mg, 0.03 mmol). The pure product was gained as a dark orange oil. (303 mg, 65%) (400MHz, CDCl₃): δ 7.47 (dd, ${}^{3}J_{H+H} = 7.6, 1.6, 1H, Ar-H$), 7.30 (t, ${}^{3}J_{H+H} = 8, 1H, Ar-H$), 7.17 (d, 1H, Ar-H), 7.10 (dt, ${}^{3}J_{H+H} = 8.0, 1.2, 1H, Ar-H$), 4.52 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2, 2H, Cp-H$), 4.50 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2, 2H, Cp-H$), 4.30 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2, 2H, Cp-H$), 4.27 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2, 2H, Cp-H$), 2.53 (s, 3H, S-Me). 13 C NMR (400 MHz, CDCl₃): δ 110.1 (1C, C-SMe), 132.3 (1C, Ar-C-H_o), 128.5 (1C, Ar-C-H_m), 124.3 (1C, Ar-C-H_o), 124.1 (1C, Ar-C-H_p), 121.9 (1C, Ar-C-C=C), 94.0 (1C, Ar-C=C), 84.1 (1C, Ar-C=C-Fc), 76.6 (2C, Cp-C-H), 74.4 (2C, Cp-C-H), 72.5 (2C, Cp-C-H), 71.4 (2C, Cp-C-H), 67.2(1C, Cp-C-C), 40.7 (1C, Cp-C-C), 15.2 (1C, -SMe) MS ES+: m/z 458.9, ([M+H]+ Calc.: 458.9) (Found: C, 49.80; H, 3.42. Calc. for C₃₆H₂₆Fe₂ C, 49.80; H, 3.30.)

Synthesis of 1-iodo,1'-(3-thioanisole)ethynylferrocene (1.4): Method repeated as for **1.1** with 1,1'-diiodoferrocene (0.96 g, 2.19 mmol), DIPA (2 ml), 3-ethynylthioanisole (65 mg, 0.44 mmol), Cul (3.3 mg, 0.02 mmol) and Pd(P^tBu₃)₂ (6.8 mg, 0.01 mmol). The pure product was gained as a dark orange oil (170 mg, 84%). (400MHz, CD₂Cl₂): δ 7.37 (bs, 1H, Ar-*H*_o), 7.29-7.17 (m, 3H, Ar-H), 4.46 (pseudo-t, ³J_{α,β} =2, 2H, Cp-H), 4.45 (pseudo-t, ³J_{α,β} =2, 2H, Cp-H), 4.28 (pseudo-t, ³J_{α,β} =2, 2H, Cp-H), 4.24 (pseudo-t, ³J_{α,β} =2, 2H, Cp-H), 2.49 (s, 3H, S-Me). ¹³C NMR (400 MHz, CD₂Cl₂): δ139.5 (1C, C-SMe), 129.1 (1C, Ar-C-H_o), 129.1 (1C, Ar-C-H), 128.2 (1C, Ar- C-H), 126.3 (1C, Ar-C-H), 124.9 (1C, Ar-C-C=C), 87.9 (1C, -C=C-), 86.7 (1C, -C=C-), 76.8 (2C, Cp-C-H), 74.5 (2C, Cp-C-H), 72.5 (2C, Cp-C-H), 71.3 (2C, Cp-C-H), 67.8 (1C, Cp-C-C), 41.6 (1C, Cp-

C-I), 15.8 (1C, -SMe). MS ES+: m/z 457.931, ([M]+ Calc.: 457.93) (Found: C, 49.80; H, 3.38. Calc. for $C_{36}H_{26}Fe_2$ C, 49.80; H, 3.30.)

Synthesis of 1-iodo,1'-(4-thioanisole)ethynylferrocene (1.5): Method repeated as for 1.1 with 1,1'-diiodoferrocene (2.40 g, 5.50 mmol), DIPA (11.5 ml), 4-ethynylthioanisole (163 mg, 1.10 mmol), Cul (8.15 mg, 0.04 mmol) and Pd(P(¹Bu)₃)₂ (16.8 mg, 0.03 mmol). The pure product was gained as a dark orange oil (383 mg, 76%). (400 MHz, CDCl₃): \bar{o} 7.43 (d, ${}^{3}J_{H-H} = 8.4$, 2H, ArH₀), 7.19 (d, ${}^{3}J_{H-H} = 8.4$, 2H, ArH), 4.47 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2$, 2H, Cp-H), 4.45 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2$, 2H, Cp-H), 4.26 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2$, 2H, Cp-H), 4.23 (pseudo-t, ${}^{3}J_{\alpha,\beta} = 2$, 2H, Cp-H), 2.50 (s, 3H, S-Me).¹³C NMR (400 MHz, CDCl₂): \bar{o} 138.8 (1C, C-SMe), 131.9 (2C, Ar-C-H), 126.1 (2C, Ar-C-H), 120.3 (1C, Ar-C-C=C), 87.2 (1C, -C=C-), 86.8 (1C, -C=C-), 76.5 (2C, Cp-C-H), 74.1 (2C, Cp-C-H), 72.1 (2C, Cp-C-H), 71.0 (2C, Cp-C-H), 67.9 (1C, Cp-C-C), 41.4 (1C, Cp-C-I), 15.7 (1C, -SMe). MS ES+: m/z 457.9, ([M]+ Calc.: 457.93), (Found: C, 49.74; H, 3.18. Calc. for C₃₆H₂₆Fe₂ C, 49.80; H, 3.30.)

Synthesis of 1,1"'-bisphenylethynylbiferrocene (2.1): 1-lodo,1'phenylethynylferrocene (214 mg, 0.49 mmol) and N-methyl-2-pyrrolidone (4 ml) were placed under a N₂ environment and degassed for 10 min. Copper(I) thiophene-2-carboxylate (423 mg, 2.22 mmol) was added against a flow of N2 and the solution was stirred overnight. The solution was filtered through celite and washed with DCM. The majority of the solvent was removed in vacuo. The remaining solvent was removed by dissolving the product in ethyl acetate and washing with brine (3 x 50 ml). The organic layer was dried with MgSO4, filtered and the solvent was removed. The product was purified by chromatography on a silica column with *n*-hexane/DCM ([1:0] \rightarrow [0:1] v/v). This gave the product as an orange solid (95 mg, 69%). ^1H NMR (400 MHz, CDCl_3): δ 7.43 (m, 4H), 7.30 (m, 6H), 4.43 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =2, 4H), 4.27 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =2, 4H), 4.23 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =2, 4H), 4.07 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =2, 4H). ${}^{13}C$ NMR (400 MHz, CDCl₃): δ 131.5 (2C), 128.4 (2C), 127.6 (1C), 72.8 (4C), 70.1 (4C), 69.9 (4C), 68.5 (4C). MS ES+: m/z 570.1. ([M]⁺ Calc.: 570.1) (Found: C, 75.70; H, 4.47. Calc. for C₃₆H₂₆Fe₂ C, 75.82; H, 4.60.)

Synthesis of 1,1"'**-bis(3-pyridyl)ethynylbiferrocene (2.2):** Method repeated as for **2.1** with 1-lodo,1'-(3-pyridyl)ethynylferrocene, (205 mg, 0.48 mmol) N-methyl-2-pyrrolidone (4 ml), copper(I) thiophene-2-carboxylate (454 mg, 2.38 mmol) This gave the product as an orange solid. (10 mg, 15%) ¹H NMR (400 MHz, CDCl₃): δ 8.63 (s, 2H), 8.50 (s, 2H), 7.66 (dt, ${}^{3}J_{H+H}$ =7.9, 1.9, 2H), 7.24-7.21 (m, 2H), 4.42 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =1.9, 4H), 4.29 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =1.9, 4H), 4.21 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =1.9, 4H), 4.21 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =1.9, 4H), 4.11 (pseudo-t, ${}^{3}J_{\alpha,\beta}$ =1.9, 4H). ¹³C NMR (400 MHz, CDCl₃): δ 152.2 (2C), 147.9 (2C), 138.2 (2C), 123.0 (2C), 84.4 (2C), 82.9 (2C), 77.4 (2C), 72.9 (4C), 70.3 (4C), 69.8 (4C), 68.3 (4C). MS ES+: m/z 573.0, ([M+H]⁺ Calc.: 573.1) (Found: C, 71.19 H, 4.09 N, 4.97. Calc. for C₃₆H₂₆Fe₂ C, 71.36; H, 4.23; N, 4.90.)

Synthesis of 1,1"'-bis(1,2'-thioanisole)ethynylbiferrocene (2.3): Method repeated as for **2.1** with 1-iodo,1'-(2-thioanisole)ethynylferrocene (221 mg, 0.48 mmol), N-methyl-2-pyrrolidone (4 ml), Copper(I) thiophene-2-carboxylate (462 mg, 2.42 mmol). This gave the product as an orange solid (85 mg, 53%). ¹H NMR (400MHz, CDCl₃): δ 7.39 (dd, ³J H-H = 7.6, 1.6, 2H, Ar-H), 7.27 (td, ³J H-H = hidden by CHCl₃, 2H, Ar-H), 7.15 (qd, 2H, Ar-H), 7.27 (td, ³J H-H = 7.6, 1.2, 2H, Ar-H), 4.50 (pseudo-t, ³J_{α,β} = 2, 4H, Cp-H), 4.31 (pseudo-t, ³J_{α,β} = 2, 4H, Cp-H), 4.31 (pseudo-t, ³J_{α,β} = 2, 4H, Cp-H), 4.29 (pseudo-t, ³J_{α,β} = 2, 4H, Cp-H), 4.08 (pseudo-t, ³J_{α,β} = 2, 4H, Cp-H), 122.3 (2C, Ar-C-H), 124.3 (2C, Ar-C-H), 124.2 (2C, Ar-C-H), 122.3 (2C, Ar-C-C=C), 95.2, 84.60, 83.3, 77.4, 72.9 (4C, Cp-C-H), 70.5 (4C, Cp-C-H), 70.3 (4C, Cp-C-H), 68.7 (4C, Cp-C-H), 65.7, 15.2 (2C, -SMe) MS ES+: m/z 662.0, ([M]+ Calc.: 662.05) (Found: C, 68.71; H, 4.37. Calc. for C₃₆H₃₀Fe₂S₂ C, 68.90; H, 4.56.)

Synthesis of 1,1"'-bis(1,3'-thioanisole)ethynylbiferrocene (2.4): Method repeated as for **2.1** with 1-iodo,1'-(3-thioanisole)ethynylferrocene (103 mg, 0.23 mmol), N-methyl-2-pyrrolidone (4 ml), Copper(I) thiophene-2-carboxylate (214 mg, 1.12 mmol). This gave the product as an orange solid (53 mg, 71%). ¹H NMR (400MHz, CDCl₃): δ 7.30 (bs, 2H, Ar-*H*_o), 7.24-7.16 (m, 6H, ArH), 4.43 (pseudo-t, ³*J*_{α,β} = 2, 4H, Cp- H), 4.27 (pseudo-t, ³*J*_{α,β} = 2, 4H, Cp- H), 4.23 (pseudo-t, ³*J*_{α,β} = 2, 4H, Cp- H), 4.27 (pseudo-t, ³*J*_{α,β} = 2, 4H, Cp-H), 2.51 (s, 6H, S-Me). ¹³C NMR (400 MHz, CDCl₃): δ138.7 (2C, C-SMe), 129.0 (2C, Ar-C-H), 128.7 (2C, Ar-C-H), 128.1 (2C, Ar- C-H), 125.8 (2C, Ar-C-H), 124.9 (2C, Ar-C-E), 88.9 (2C, -C≡C-), 85.7 (2C, -C≡C-), 84.4 (2C, Cp-C-C), 72.8 (4C, Cp-C-H), 70.2 (4C, Cp-C-H), 69.9 (4C, Cp-C-H), 68.4 (4C, Cp-C-H), 65.9 (2C, Cp-C-C), 15.9 (2C, -SMe) MS ES+: m/z 662.0485, [[M]+ Calc.: 662.05) (Found: C, 69.08; H, 4.69. Calc. for C₃₆H₃₀Fe₂S₂ C, 68.90; H, 4.56.)

Synthesis of 1,1^{,,1}-bis(1,4'-thioanisole)ethynylbiferrocene (2.5): Method repeated as for 2.1 with 1-iodo,1'-(4-thioanisole)ethynylferrocene (383 mg, 0.84 mmol), N-Methyl-2-pyrrolidone (15 ml), Copper(I) thiophene-2-carboxylate (797 mg, 4.18 mmol). This gave the product as an orange solid (115.7 mg, 42 %). ¹H NMR (400MHz, CDCl₃): $\overline{0}$ 7.33 (d, ³J_{H-H} =8.6, 4H, Ar-*H*₀), 7.16 (d, ³J_{H-H} =8.6, 4H, Ar -*H*_m), 4.41 (pseudo-t, ³J_{\alpha\beta} =2, 4H, Cp-*H*), 4.24 (pseudo-t, ³J_{\alpha\beta} =2, 4H, Cp-*H*), 4.27 (pseudo-t, ³J_{\alpha\beta} =2, 4H, Cp-*H*), 4.07 (pseudo-t, ³J_{\alphaβ} =2, 4H, Cp-*H*), 2.50 (s, 6H, S-

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A new methodology for the synthesis and incorporation of biferrocenyl systems within extended conjugated systems is reported, alongside indepth cyclic voltammetry, UV/vis/NIR spectroelectrochemistry and X-ray crystallography characterisation.

Key Topic*

Lucy E. Wilson, Christopher Hassenrück, Rainer F. Winter, Andrew J.P White, Tim Albrecht* and Nicholas J. Long *

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Functionalised biferrocene systems towards molecular electronics

*biferrocenes, electronic materials

