

# Synthesis and characterisation of aromatic ethynyl-bridged ferrocenes

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## Abstract

A series of aromatic ethynyl-bridged ferrocenes with the general formula  $\text{Fc-C}\equiv\text{C-R-C}\equiv\text{C-Fc}$  ( $\text{Fc}$  = ferrocenyl,  $\text{R} = \text{C}_6\text{H}_2(-p\text{-CH}_3)_2$  (**1**),  $\text{C}_6\text{H}_4-p\text{-C}_6\text{H}_4$  (**2**),  $\text{C}_5\text{H}_3\text{N}$  (**3**),  $9,10\text{-C}_{14}\text{H}_8$  (**4**),  $\text{C}_4\text{H}_2\text{S}$  (**5**),  $(\text{C}_4\text{H}_2\text{S})_2$  (**6**) and  $(\text{C}_4\text{H}_2\text{S})_3$  (**7**)) has been synthesised by the reaction of ethynyl ferrocene with the appropriate dibromo-arenes. The new complexes have been characterised by spectroscopic techniques. The structures of **3** and **7** were determined via X-ray crystallography, and both show the *trans-trans* configuration of the two ethynyl ferrocene groups with respect to the central R group. The electronic properties of the compounds have been studied via optical spectroscopy and cyclic voltammetry.

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**Keywords:** Ethynyl ferrocenes; Cyclic voltammetry; X-ray crystallography; Optical spectroscopy

## 1. Introduction

Research into the synthesis and electronic properties of metal ethynyl complexes and polymers continues to develop as a key area of organometallic chemistry [1]. The complexes and polymers are composed of transition metals, auxiliary alkylphosphines and linear ethynyl ligands with aromatic or hetero-aromatic spacer groups (Fig. 1) [1]. Their rigid-rod architectures [2] and conjugated backbones [3] make them useful materials in the field of linear [4] and non-linear optics [5], liquid crystallinity [6] and photovoltaic cells [4a,7]. Since the discovery of rigid-rod Group 10 metal (Pt, Pd and Ni) ethynyl complexes and polymers, an active area of research has involved the discovery of new routes [1h,8] for the synthesis of new materials containing a wide range of transition metals.

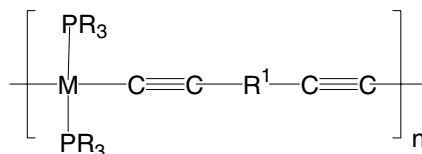
Ferrocene is a well-known redox active material and can be incorporated into metal ethynyl complexes and polymers as a redox active centre [1b,1c,1f,9]. A number of ferrocenyl complexes and polymers with Ru [10], Os [10], Mn [11], Ni [12], Pd [12], Pt [13] and Au [14] cores have been synthesised and studied for their electronic communication behaviour. Recently, we reported the synthesis of platinum ethynyl complexes and polymers with ferrocene either in the main chain of the polymers [13b] or as a pendant group (Fig. 2) [13d]. We, herein, report the synthesis of ethynyl-bridged ferrocenes with aromatic and heterocyclic spacers.

## 2. Results and discussion

In our first attempt to synthesise aromatic ethynyl-bridged ferrocenes, iodoferrocene was reacted with appropriate *bis* ethynyl ligands in the presence of  $\text{Pd}^0/\text{Cu}^{\text{I}}$  catalysts (Scheme 1, Route A). After 48 h under reflux in diisopropylamine, the reaction had not gone to completion as indicated by IR and  $^1\text{H}$  NMR spectroscopy.

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M = Pt, Pd and Ni; R = alkyl groups; R<sup>1</sup> = aromatic or heterocyclic groups

Fig. 1. General structure of group 10 metal polyalkynyls.

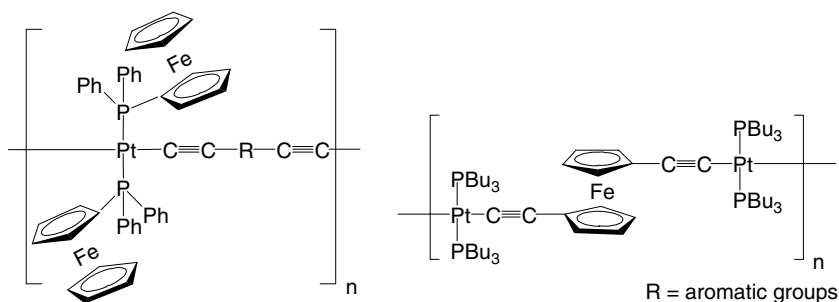
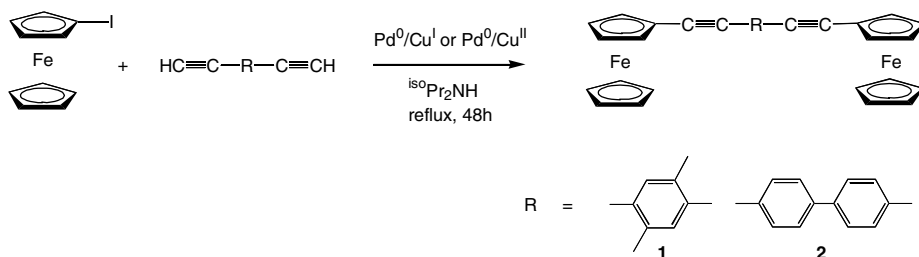
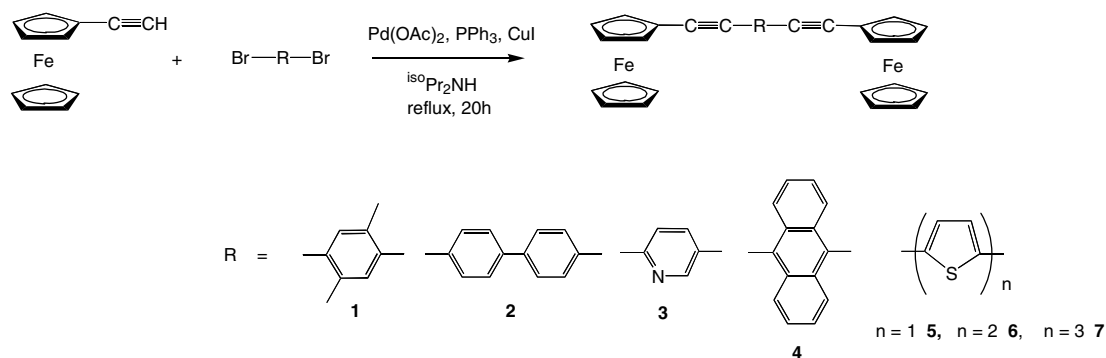


Fig. 2. Examples of platinum polyalkynyls with ferrocene units in the main chain or as pendant groups.

#### Route A



#### Route B

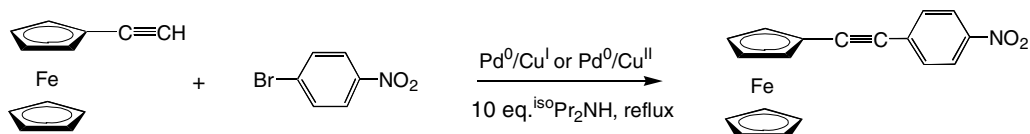


Scheme 1. Formation of compounds 1–7 (routes A and B).

The yield of the reactions was increased when Pd<sup>0</sup>/Cu<sup>II</sup> were used as catalysts instead of Pd<sup>0</sup>/Cu<sup>I</sup>. Chromatographic separations of the crude residues afforded 30–40% of the pure products as well as the iodoferrocene starting material.

A cleaner reaction was obtained when ethynylferrocene was reacted with dibromoaromatic compounds

(Scheme 1, Route B). The reactions were completed at 50–60 °C in diisopropylamine in the presence of Pd<sup>0</sup>/Cu<sup>I</sup> or Pd<sup>0</sup>/Cu<sup>II</sup> catalysts. The reaction of ethynylferrocene with 4-bromonitrobenzene (Scheme 2) was studied by IR spectroscopy to understand the kinetics of such reactions, i.e., using Pd<sup>0</sup>/Cu<sup>I</sup> or Pd<sup>0</sup>/Cu<sup>II</sup> catalysts. The reactions were carried out in dichloromethane using a



Scheme 2. Reaction of ethynylferrocene and 4-bromonitrobenzene.

10-fold excess of  $i\text{Pr}_2\text{NH}$  under reflux, and IR spectra of the reactions were recorded every 10 min. The IR absorption of  $\nu(\text{C}\equiv\text{C}-\text{H})$  fragments at ca.  $3300\text{ cm}^{-1}$  was plotted against time (Fig. 3). The absorbance decreases more rapidly when using  $\text{Cu}^{\text{II}}$  catalysts than for  $\text{Cu}^{\text{I}}$  thus indicating that the reactions catalysed by  $\text{Pd}^0/\text{Cu}^{\text{II}}$  proceed much faster than those with  $\text{Pd}^0/\text{Cu}^{\text{I}}$  species. This result is consistent with the reports of Sato et al. [15] where it has been observed that the Pd/Cu catalysed cross-coupling reactions were accelerated by the oxidatively induced reductive eliminations in the palladium metal centres (Fig. 4).

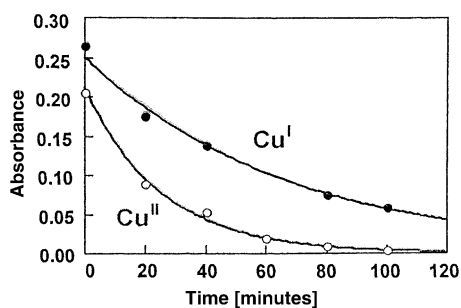


Fig. 3. Plot of absorbance vs. time for the reaction of  $\text{Fc}-\text{C}\equiv\text{CH}$  and  $\text{Br}-\text{Ph}-4-\text{NO}_2$ . Absorbance was monitored at the wave number  $3300\text{ cm}^{-1}$ .

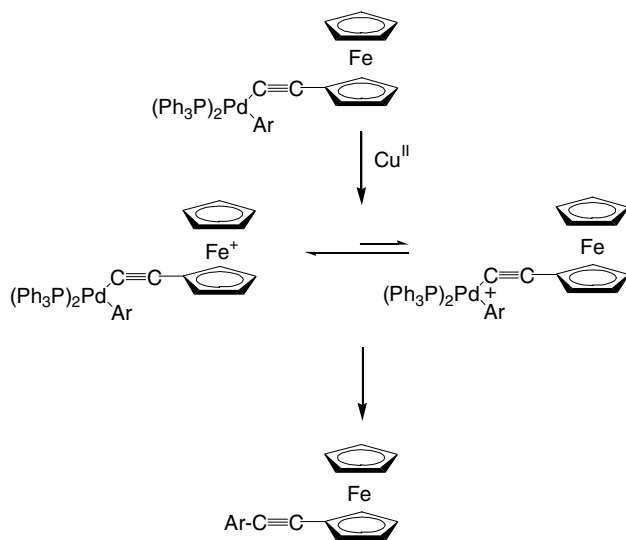


Fig. 4. Mechanism for oxidatively induced reductive eliminations at palladium centres.

Though faster, the use of  $\text{Pd}^0/\text{Cu}^{\text{II}}$  catalysts resulted in lower yields of the pure products due to decomposition (the colour of the reaction mixture changed from yellow to black), thus compounds **1–7** were synthesised using  $\text{Pd}^0/\text{Cu}^{\text{I}}$  catalysed cross-coupling reactions between ethynylferrocene and dibromoaryl precursors (Scheme 1, Route B) (i.e., for **5**, the isolated yield using  $\text{Cu}^{\text{II}}$  catalysts is 50% but using  $\text{Cu}^{\text{I}}$  it is 71%). The crude products were purified via column chromatography on silica and isolated as yellow to red-brown air-stable solids in 50–90% yield. All the complexes were characterised by microanalysis, IR and NMR spectroscopy and mass spectrometry. The complexes **1–7** displayed IR bands at  $\sim 2210\text{ cm}^{-1}$  which are diagnostic of the ferrocenylethynyl moiety [10c,13e,16]. In the  $^1\text{H}$  NMR spectra of the complexes, a pattern of singlets and triplets centred at  $\sim 4\text{ ppm}$  were observed due to the presence of unsubstituted and substituted cyclopentadienyl ligands, respectively [10c]. The aromatic spacers displayed peaks as singlets, doublets and complex multiplets in the  $^1\text{H}$  NMR spectra of the compounds in the expected 7–8 ppm regions. Mass spectrometry (FAB +ve) displayed the presence of molecular ions with characteristic fragmentation patterns for the complexes.

It should be noted that during the course of this work, the syntheses of **5**, **6** and **7** were reported by Lin and co-workers [17]. The same synthetic methods were applied and similar product yields were obtained (77%, 48% and 66% for **5**, **6** and **7**, respectively) and the monothiophene species **5** was characterised by X-ray crystallography.

We carried out structural analysis of compounds **3** and **7**. The molecular structure of **3** is illustrated in Fig. 5. There is a crystallographically imposed inversion centre in the middle of the pyridyl ring and thus the position of the nitrogen atom is consequently disordered 50:50 over the N(1) and the C(15) positions. The complex has an extended conformation, the two ethynyl linkages being essentially linear [the angles at C(11) and C(12) being  $178.4(3)^\circ$  and  $178.2(3)^\circ$ , respectively], with a C(11)···C(11A) separation of ca.  $8.00\text{ \AA}$ . The  $\text{C}_5\text{H}_4$  rings are nearly coplanar with the central pyridyl ring, being inclined by ca.  $8^\circ$ . The ferrocenyl units have eclipsed conformations, the two  $\text{C}_5$  rings being staggered by only ca.  $2^\circ$  and inclined to each other by ca.  $2^\circ$ . Adjacent molecules are linked end-to-middle by a  $\text{C}-\text{H}\cdots\pi$  interaction from C(14)–H to the centre of the C(1)–C(5) cyclopentadienyl ring [ $\text{H}\cdots\pi$   $2.61\text{ \AA}$ ,  $\text{C}-\text{H}\cdots\pi$

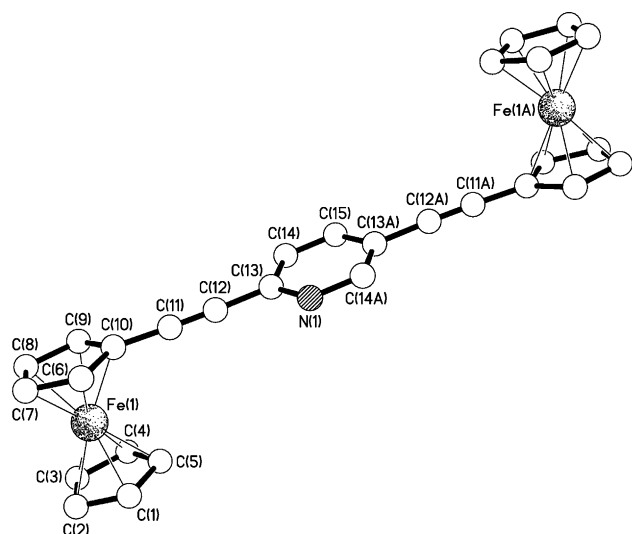


Fig. 5. The molecular structure of **3**. Selected bond lengths (Å) and angles (°); C(11)–C(12) 1.169(4), C(10)–C(11)–C(12) 178.4(3) and C(11)–C(12)–C(13) 178.2(3).

165°] to form a continuous chain that extends in the crystallographic  $10\bar{1}$  direction.

A single crystal structure analysis showed compound **7** to have approximate non-crystallographic  $C_s$  symmetry about a plane perpendicular to the central thiophene ring, passing through S(2) and the centre of the C(8)–C(9) bond (Fig. 6). The bisethynyl-trithiophene unit has a typical extended geometry with alternating orientations of the three thiophene rings. The maximum departure from linearity in the ethynyl units is only ca. 4°. The distance between the two ethynyl carbon atoms C(1) and C(16) is 15.3 Å, a value very similar to those observed in the related structures, 5,5''-bis((5-*n*-buty-

lthien-2-yl)ethynyl)-2,2' : 5',2''-terthiophene, (15.2 Å) [18] and ( $\mu_2$ -5,5''-bis(2-ethynyl)-2,2' : 5',2''-trithiophene)-bis(triphenylphosphine)-di-gold(I) (15.4 Å) [19]. The central trithiophene unit is non-planar, there being torsional twists, in opposite senses, of ca. 7° and 5° about the C(6)–C(7) and C(10)–C(11) bonds, respectively; the C(21) and C(31)-containing cyclopentadienyl rings are inclined by ca. 14° and 7°, respectively, to their adjacent thiophene rings. The Fe(1) ferrocenyl has an almost perfectly eclipsed geometry with its rings inclined by ca. 2°, whilst that for Fe(2) has a ca. 10° stagger (rings inclined by ca. 1°). Centrosymmetrically related pairs of molecules are  $\pi$ -stacked 'face-to-face', the mean interplanar and centroid–centroid separations of their central thiophene rings being 3.60 and 3.91 Å, respectively; the equivalent values for the terminal cyclopentadienyl rings are 4.09 and 3.81 Å. These 'dimer' pairs pack 'end-to-middle' and interlock to form mosaic-like sheets (Fig. 7). There are no inter-sheet interactions of note.

In the UV–Vis spectra of all the complexes, intense absorption bands were observed at ~300–400 nm (Fig. 8) that can be assigned to  $\pi$ – $\pi^*$  transitions of the conjugated ligands [17]. Ethynyl ligands and their metal complexes are good candidates for photoluminescence studies [4b,4c] and we have studied the photoluminescence spectra of complex **6** and the corresponding ethynyl ligand,  $\text{Me}_3\text{SiC}\equiv\text{C}-(\text{C}_4\text{H}_2\text{S})_2-\text{C}\equiv\text{CSiMe}_3$ . Although the ligand displayed photoluminescence at 550 nm (Fig. 9), no such emissions were observed in the ferrocene ethynyl complex **6** under similar conditions. The emission of aromatic ethynyl ligands may be diminished due to the quenching effects of the ferrocene moiety [14].

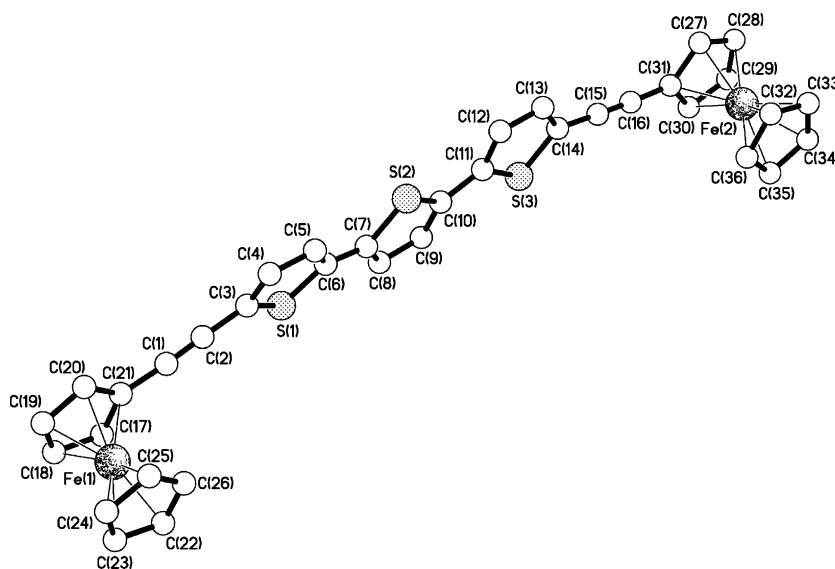


Fig. 6. The molecular structure of **7**. Selected bond lengths (Å) and angles (°); C(1)–C(2) 1.184(9), C(15)–C(16) 1.176(8), C(21)–C(1)–C(2) 176.8(7), C(1)–C(2)–C(3) 175.8(6), C(14)–C(15)–C(16) 178.2(7) and C(15)–C(16)–C(31) 177.0(6).

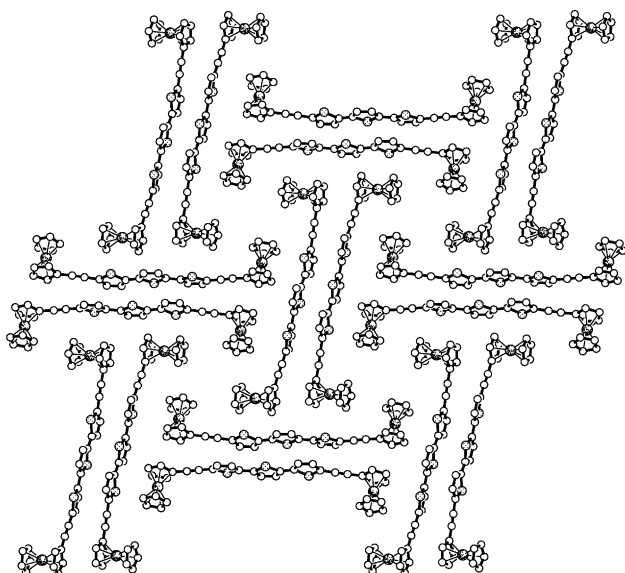


Fig. 7. Part of one of the sheets of interlocked face-to-face 'dimer' pairs in the structure of 7.

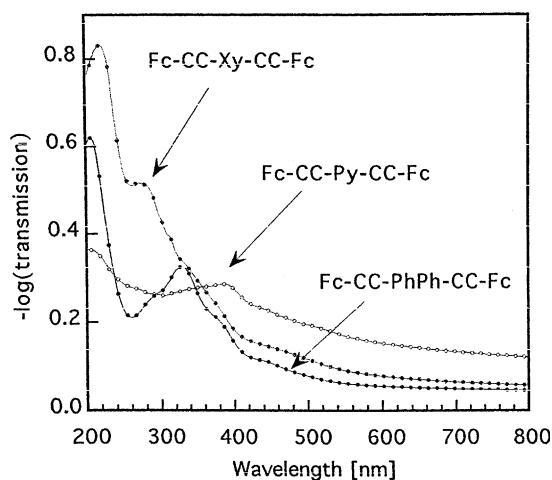


Fig. 8. Absorption spectra of the compounds 1–3.

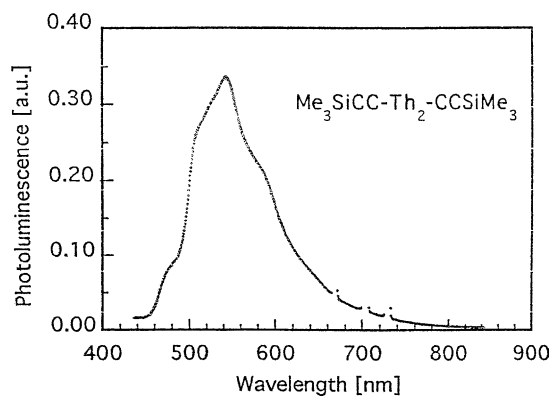


Fig. 9. Photoluminescence spectrum of the ligand  $\text{Me}_3\text{SiC}\equiv\text{C}-(\text{Th})_2\text{C}\equiv\text{C}-\text{SiMe}_3$ .

Table 1  
Electrochemical data for  $\text{Fc}-\text{C}\equiv\text{C}-\text{R}-\text{C}\equiv\text{C}-\text{Fc}$  system (compounds 1–4)

Compounds	$E_{1/2\text{STD}}$ (V)	$\Delta E = E_{\text{pa}} - E_{\text{pc}}$ (V)	$I_{\text{pa}}/I_{\text{pc}}$
1	0.20	140	0.65
2	0.19	150	0.72
3	0.17	180	0.73
4	0.18	110	0.61

All the potentials were referenced to  $\text{Fc}/\text{Fc}^+$  redox couple ( $\text{Fc}/\text{Fc}^+ = 0.45 \text{ V vs. Ag}/\text{Ag}^+$ ).  $\Delta E$  for ferrocene is 110 mV.  $I_{\text{pa}}/I_{\text{pc}}$  for ferrocene is 0.73.

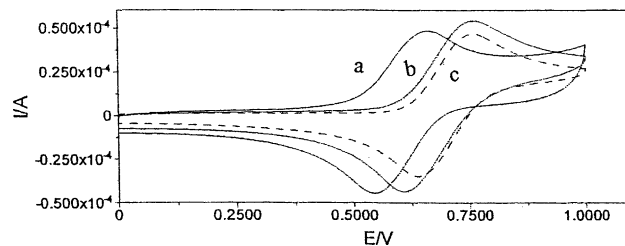


Fig. 10. Cyclic voltammograms of the compounds 4 (a), 1 (b) and 5 (c).

Cyclic voltammetric studies of compounds 1–7 were performed using a three-electrode system with Pt as a working electrode, Pt as an auxiliary electrode and  $\text{Ag}/\text{Ag}^+$  as a reference electrode (Table 1). Cyclic voltammograms of the ethynyl-bridged ferrocenes displayed one quasi-reversible wave (Fig. 10) which is due to oxidation of the ferrocene moiety [10c]. This suggests that there are no Fe–Fe interactions in the dimetallic complexes 1–7 through the conjugated aryl ethynyl bridges. This result is consistent with previous studies in similar ethynyl-bridged fluorene systems [16]. However, Fe–Fe interactions were observed in ethynyl-bridged ferrocenes of the type  $\text{Fc}-(\text{C}\equiv\text{C})_n-\text{Fc}$  by cyclic voltammetry [20]. In the cyclic voltammogram of  $\text{Fc}-\text{C}\equiv\text{C}-\text{Fc}$ , two one-electron oxidations were observed, and the separation between the waves was 130 mV indicating moderate metal–metal interaction. However, in the case of  $\text{Fc}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Fc}$ , the waves are separated by 100 mV suggesting that the Fe–Fe interaction decreases with increasing bridge length. No significant variation of  $E_{1/2}$  was observed in 1–7 due to the presence of electron-rich or electron-withdrawing spacers. However, the oxidation of iron centres becomes more anodic compared to ferrocene due to the removal of electron density by the aromatic and heterocyclic spacers through the ethynyl bridges [13c].

### 3. Experimental

#### 3.1. General

All the reactions were performed strictly under nitrogen atmospheres using standard Schlenk techniques

[21]. Solvents were freshly dried and distilled with appropriate drying agents before use [21]. IR spectra were recorded as dichloromethane solutions, in NaCl cells, using a Mattson Polaris Fourier Transform IR spectrometer.  $^1\text{H}$  NMR spectra were recorded on a JEOL EX270 MHz spectrometer. Chemical shifts are reported in ppm using  $\text{CDCl}_3$  ( $^1\text{H}$ , 7.25 ppm) as the reference. Mass spectra were recorded using positive FAB methods on an Autospec Q mass spectrometer. Microanalysis was performed at SACS, University of North London, UK. The electrochemical investigations were carried out at 298 K using 0.1 M  $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{CH}_2\text{Cl}_2$  as supporting electrolyte under an  $\text{N}_2$  atmosphere. All the electrochemical measurements were referenced against the ferrocene/ferrocenium redox couple ( $E_{1/2} = 0.45$  vs.  $\text{Ag}/\text{Ag}^+$  at 298 K in  $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{CH}_2\text{Cl}_2$ ).

### 3.2. X-ray crystallography

*Crystal data for 3:*  $\text{C}_{29}\text{H}_{21}\text{NFe}_2$ ,  $M = 495.16$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 7.4490(2)$ ,  $b = 13.0026(3)$ ,  $c = 11.2875(4)$  Å,  $\beta = 106.4810(10)^\circ$ ,  $V = 1048.35(5)$  Å<sup>3</sup>,  $Z = 2$  [ $C_i$  symmetry],  $D_c = 1.569$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 1.401$  mm<sup>-1</sup>,  $T = 180$  K, orange irregular blocks; 3050 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.042$ ,  $wR_2 = 0.112$ , 2489 independent observed absorption corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ],  $2\theta_{\text{max}} = 60^\circ$ ], 152 parameters. CCDC 228078.

*Crystal data for 7:*  $\text{C}_{36}\text{H}_{24}\text{S}_3\text{Fe}$ ,  $M = 608.58$ , monoclinic,  $P2_1/c$  (no. 14),  $a = 6.0084(3)$ ,  $b = 25.4032(14)$ ,  $c = 18.7475(10)$  Å,  $\beta = 90.349(4)^\circ$ ,  $V = 2861.4(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.413$  g cm<sup>-3</sup>,  $\mu(\text{Cu K}\alpha) = 6.453$  mm<sup>-1</sup>,  $T = 293$  K, orange prisms; 4220 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.049$ ,  $wR_2 = 0.096$ , 2897 independent observed absorption corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ],  $2\theta_{\text{max}} = 120^\circ$ ], 371 parameters. CCDC 228079.

### 3.3. Synthesis

Iodoferrocene [22], ethynyl ferrocene [23], 2,5-bis(ethynyl)-*p*-xylene and 4,4-bis(ethynyl)biphenyl [24] were prepared following literature methods. All other materials were purchased from the Aldrich Chemicals Company.

#### 3.3.1. 1,4-Bis-(ferrocenylethynyl)-*p*-xylene (1)

Ethynylferrocene (0.23 g, 1.1 mmol), 1,4-dibromo-*p*-xylene (0.13 g, 0.5 mmol) were heated under reflux for 20 h in diisopropylamine (40 ml) in the presence of  $\text{CuI}$  (4 mg),  $\text{Pd}(\text{OAc})_2$  (5 mg) and  $\text{Ph}_3\text{P}$  (10 mg) during which time a reddish-brown precipitate appeared. The solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel using dichloromethane/hexane as eluants. The pure product (0.18 g) was isolated as a yellow solid in 69% yield. Anal.

Calc. for  $\text{C}_{32}\text{H}_{26}\text{Fe}_2$ : C, 73.61; H, 4.98. Found: C, 73.59; H, 4.98%. IR ( $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2211.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.42 (s, 6H,  $\text{CH}_3$ ), 4.24 (br s, 14H,  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{H}_4$ ), 4.49 (t, 4H,  $\text{C}_5\text{H}_4$ ), 7.29 (s, 2H,  $\text{C}_6\text{H}_2$ ). FAB +ve;  $m/z$ : 522  $[\text{M}]^+$ .

#### 3.3.2. 4,4-Bis-(ferrocenylethynyl)biphenyl (2)

Following the procedure for **1**, but using 4,4-dibromobiphenyl gave **2** as a brown solid (0.18 g) in 64% yield. Anal. Calc. for  $\text{C}_{36}\text{H}_{26}\text{Fe}_2$ : C, 75.83; H, 4.46. Found: C, 75.72; H, 4.58%. IR ( $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2208 (s), 2222 (w).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.25 (br s, 14H,  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{H}_4$ ), 4.50 (t, 4H,  $\text{C}_5\text{H}_4$ ), 7.55 (br s, 8H,  $\text{C}_6\text{H}_4$ ). FAB +ve;  $m/z$ : 570  $[\text{M}]^+$ .

#### 3.3.3. 2,5-Bis-(ferrocenylethynyl)pyridine (3)

As for the formation of **1**, but using 2,5-dibromopyridine gives **3** as a red-brown solid (0.21 g) in 87% yield. Anal. Calc. for  $\text{C}_{29}\text{H}_{21}\text{NFe}_2 \cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 68.03; H, 4.16; N, 2.71. Found: C, 67.98; H, 4.25; N, 2.42%. IR ( $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2204 (w), 2223 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.20 (s, 10H,  $\text{C}_5\text{H}_5$ ), 4.45 (t, 4H,  $\text{C}_5\text{H}_4$ ), 4.52 (t, 4H,  $\text{C}_5\text{H}_4$ ), 7.35 (d, 1H,  $\text{C}_6\text{H}_3\text{N}$ ), 7.63 (d, 1H,  $\text{C}_6\text{H}_3\text{N}$ ), 8.60 (s, 1H,  $\text{C}_6\text{H}_3\text{N}$ ). FAB +ve;  $m/z$ : 495.1  $[\text{M}]^+$ .

#### 3.3.4. 9,10-Bis-(ferrocenylethynyl)anthracene (4)

The same procedure as used for **1**, but with 9,10-dibromoanthracene gives **4** as a red-brown solid (0.17 g) in 58% yield. Anal. Calc. for  $\text{C}_{38}\text{H}_{26}\text{Fe}_2 \cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 74.63; H, 4.30. Found: C, 74.97; H, 4.40%. IR ( $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}\equiv\text{C})$  2199.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.33 (s, 10H,  $\text{C}_5\text{H}_5$ ), 4.36 (br s, 4H,  $\text{C}_5\text{H}_4$ ), 4.71 (br s, 4H,  $\text{C}_5\text{H}_4$ ), 7.62 (br m, 4H, anthracene-H), 8.61 (br m, 4H, anthracene-H). FAB +ve;  $m/z$ : 594  $[\text{M}]^+$ .

Following the synthetic method for **1**, compounds **5**, **6** and **7** were synthesised in yields of 71%, 63% and 53%, respectively. However, during the course of this work, these compounds were reported by Lin and co-workers [17].

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