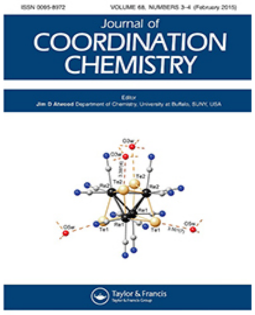

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Synthesis of tetraferrocenylbenzene by cycloaddition reaction with alkyl cobalt clusters as reaction precursors

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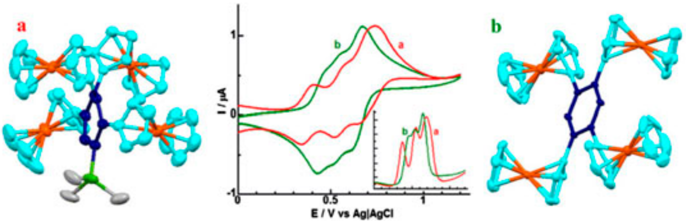

Two tetraferrocenylbenzene derivatives, 1-trimethylsilyl-2,3,4,5-tetraferrocenylbenzene (**1**) and 1,2,4,5-tetraferrocenylbenzene (**2**), were synthesized by cycloaddition reactions of alkynes with $Co_2(CO)_6(\mu^2\text{-alkyne})$ as reaction precursors and characterized by elemental analysis, FT-IR, NMR, and MS. The molecular structures of **1** and **2** were identified by single-crystal X-ray diffraction. The redox properties were studied by cyclic voltammetry and square wave voltammetry, which indicated stronger electronic communication among ferrocenyl units.

Keywords: Tetraferrocenylbenzene derivatives; Cobalt cluster; Synthesis; Crystal structures; Electrochemistry

1. Introduction

Multi-ferrocenyl aryl molecules have recently gained importance as a class of compounds that can be used for the preparation of liquid crystals [1], materials with non-linear optical properties [2], and as redox-switchable hemilabile ligands [3]. In general, the methods that have been previously used in the preparation of ferrocene aromatic compounds are summarized into two categories. One type is cycloaddition, such as the transition metal-catalyzed [2+2+2] cycloaddition with ferrocenylacetylene [4–7] and silicon tetrachloride-catalyzed [2+2+2] cycloaddition with acetylferrocene [8], the Diels–Alder [2+4] cycloaddition between tetraphenylcyclopentadienone and ferrocenylacetylene derivatives [9, 10], [3+3]

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*Corresponding author. Email: hanlimin_442@hotmail.com cyclization using 1-5-ferrocenyl-3,3-bis(methylthio)prop-2-en-1-ones as the 1,3-electrophile [11]. The *n*-ferrocenyl ($n > 3$)-substituted aryl derivatives were not obtained by this method.

Another approach is cross-coupling, such as arylation of ferrocene with aryldiazonium salts [12, 13], the Stille reaction of ferrocenyltin and halobenzenes [14], the Pd-catalyzed cross-coupling of diferrocenyl mercury with halobenzenes [15], the Suzuki reaction of ferrocenylboronic acid and phenyltriflates with $Pd[P(Ph)_3]_4$ as catalyst [16], the Negishi reaction of halobenzenes and ferrocenylzinc chloride with nickel and palladium as catalyst [17, 18]. The *n*-ferrocenyl ($n > 3$)-substituted benzene was only obtained by Negishi cross-coupling reaction which requires laborious preparation techniques.

Fortunately, Krüerke and Hübel reported the $[Co_2(CO)_8]$-catalyzed cycloaddition reactions of alkynes and described a rational catalytic mechanism (see scheme 1) [19]. Based on this mechanism, as well as our previous work on the synthesis of ferrocenylbenzene with cobalt clusters [20–22], we modified Krüerke's one-pot synthesis and turned it into a two-step method. In this article, $Co_2(CO)_6(\mu^2$-alkyne), taken as precursors, reacted with diferrocenylacetylene and ferrocenylacetylene, respectively. Two tetraferrocenylbenzene derivatives were synthesized (see scheme 2). The structures of the crowded tetraferrocenylbenzene compounds were studied and the electrochemistry of the two compounds was investigated by cyclic voltammetric and square wave voltammetric techniques.

2. Experimental

2.1. *General materials and instruments*

All operations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Octacarbonyl dicobalt and trimethylsilylacetylene were obtained from Alfa-Aesar Chem. Ferrocenylacetylene, diferrocenylacetylene, $Co_2(CO)_6(\mu^2$-trimethylsilyl acetylene), and $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) were prepared according to previously reported methods [23, 24]. Dioxane was distilled under nitrogen over sodium metal.

IR spectra were measured on a Nicolet FT-IR spectrometer using KBr pellets. Elemental analyses were carried out on an Elementar Var III-type analyzer. ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded on a Jeol–Jnm-Al 500FT-MHz spectrometer. Mass spectra were determined using a Micromass LCT instrument. The crystal structures of **1** and **2** were measured on Agilent Xcalibur Eos Gemini and Bruker SMART APEX CCD diffractometers. Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed on a CHI 760C electrochemical analyzer. Electronic spectra were recorded in dichloromethane with a UV751GD UV–visible spectrophotometer.

2.2. *Synthesis of 1-trimethylsilyl-2,3,4,5-tetraferrocenylbenzene (1)*

$Co_2(CO)_6(\mu^2$-trimethylsilylacetylene) (95.3 mg, 0.248 mM) and diferrocenylacetylene (197.0 mg, 0.500 mM) were dissolved in dioxane (10 mL) at room temperature. The solution was stirred for 3 h at 70 °C, and then cooled to room temperature. The solvent was removed in vacuum. The residues were dissolved in a minimal amount of dichloromethane and subjected to chromatographic separation on a neutral alumina column (2.0 × 30 cm). Elution with a mixture of hexane and dichloromethane (3 : 1, v/v) afforded a yellow band (**1**). Crystals of **1** were obtained by recrystallizing solid **1** from a mixture of hexane and dichloromethane. Yield: 36.2%. M.p. 159–160 °C. Anal. Calcd for $C_{49}H_{46}Fe_4Si$ (%): C, 66.40; H, 5.23. Found: C, 66.72; H, 4.98. IR (cm^{-1}, KBr): 3093m (Cp, $\nu_{C–H}$); 3030w (Ph, $\nu_{C–H}$); 2953m, 2898w (CH_3, $\nu_{C–H}$); 1633m, 1505m (Ph, $\nu_{C=C}$); 1248s ($Si(CH_3)_3$, $\delta_{C–H}$); 1112m, 1034w, 1007w (Cp, $\delta_{C–H}$); 843vs ($Si(CH_3)_3$, $\nu_{Si–C}$); 812vs (Cp, $\gamma_{C–H}$). ^1H NMR (500 MHz $CDCl_3$, δ ppm): 0.27 (s, 9H, $Si(CH_3)_3$), 3.77–5.06 (m, 36H, Cp), 7.83 (s, 1H, Ph); ^{13}C NMR (125 MHz $CDCl_3$, δ ppm): 2.50 (CH_3 carbons), 69.38, 69.53, 69.82, 69.93, 71.70, 89.45, 91.64, 92.08, 92.72 (Cp carbons), 133.18, 136.04, 137.69, 138.96 (aromatic carbons). MS ($C_{49}H_{46}Fe_4Si$) ESI: $[M]^+$ *m/z*. Calcd 886.1, found 886.2.

2.3. *Synthesis of 1,2,4,5-tetraferrocenylbenzene (2)*

$Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (112.3 mg, 0.165 mM) and ferrocenylacetylene (69.3 mg, 0.330 mM) were dissolved in dioxane (10 mL) at room temperature. The solution was stirred for 3 h at 70 °C and cooled to room temperature. The solvent was removed in vacuum. The residues were dissolved in a minimal amount of dichloromethane and subjected to chromatographic separation on a neutral alumina column (2.0 × 30 cm). Elution with a mixture of hexane and dichloromethane (3 : 1, v/v) afforded a yellow band (**2**). Crystals of **2** were obtained by recrystallizing solid **2** from a mixture of hexane and dichloromethane. Yield: 38.5%. M.p. 295–296 °C. Anal. Calcd for $C_{46}H_{38}Fe_4$ (%): C, 67.86; H, 4.70. Found: C, 67.94; H, 4.32. IR (cm^{-1}, KBr): 3089m (Cp, $\nu_{C–H}$); 3050w (Ph, $\nu_{C–H}$); 1598s, 1493m (Ph, $\nu_{C=C}$); 1108m, 1034m, 999w (Cp, $\delta_{C–H}$); 812vs (Cp, $\gamma_{C–H}$). ^1H NMR (500 MHz $CDCl_3$, δ ppm): 4.145–4.211 (m, 36H, Cp), 8.20 (s, 2H, Ph); ^{13}C NMR (125 MHz $CDCl_3$, δ ppm): 67.46, 69.64, 70.88, 88.30 (Cp carbons), 134.15, 134.60 (aromatic carbons). MS ($C_{46}H_{38}Fe_4$) ESI: $[M]^+$ *m/z*. Calcd 814.0, found 814.2.

2.4. *X-ray crystallography*

All measurements were made on Agilent Xcalibur Eos Gemini and Bruker SMART APEX CCD diffractometers equipped with graphite-monochromated Cu-Kα (λ = 1.54184 Å) and Mo-Kα (λ = 0.71073 Å) radiation. Orange single crystals of **1** (0.09 mm × 0.08 mm × 0.08 mm) and **2** (0.20 mm × 0.05 mm × 0.05 mm) were selected and mounted on a glass fiber. All data were collected using the φ and ω scan techniques. The two structures were solved by direct methods and expanded using the Fourier technique. An absorption correction based on SADABS was applied. The structure solution and refinement were performed by SHELXSL 97. The crystallographic details about data collection and structure refinements for **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. *Synthesis of 1 and 2*

If $Co_2(CO)_8$-catalyzed cycloaddition reactions of two different alkynes (trimethylsilylacetylene and diferrocenylacetylene, or diferrocenylacetylene and ferrocenylacetylene) were carried out in one pot, self-cycloaddition or co-cycloaddition occurs. The molar ratio of alkynes may be different (1 : 2 or 2 : 1) in co-cycloaddition reactions. These reactions are seldom specific, and products are varied and difficult to separate.

Table 1. Crystallographic data and structure refinement for **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{49}H_{46}Fe_4Si$	$C_{46}H_{38}Fe_4$
Formula weight	886.35	814.16
Temperature (K)	293(2)	296(2)
Wavelength (Å)	1.54184	0.71073
Crystal system, Space group	Orthorhombic, *Pbca*	Monoclinic, *P 2(1)/c*
A (Å), *b* (Å), *c* (Å)	12.1132(5), 22.7843(11), 28.7917(14)	5.8672(17), 18.686(5), 15.300(4)
A (°), *β* (°), *γ* (°)	90.00, 90.00, 90.00	90.00, 91.965(5), 90.00
Volume (Å^3), *Z*	7946.2(6), 8	1676.4(8), 4
Density (Mg/m^3)	1.482	1.613
μ (mm$^{-1)}$, *F* (0 0 0)	12.021, 3664	1.731, 836
Crystal size (mm)	0.09 × 0.08 × 0.08	0.20 × 0.05 × 0.05
θ range (°)	3.07–67.25	2.18–28.31
Limiting indices	$-7 \leq h \leq 14$, $-27 \leq k \leq 27$, $-34 \leq l \leq 34$	$-7 \leq h \leq 7$, $0 \leq k \leq 24$, $0 \leq l \leq 20$
Reflections collected	43,688	4044
Independent reflections	7117	4076
Completeness to θ	99.8%	97.0%
Max. and min.	0.4464/0.4109	0.9184/0.7234
Data/restraints/parameters	7117/1758/490	4076/0/227
Goodness-of-fit on F^2	0.999	1.040
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0633$, $wR_2 = 0.1335$	$R_1 = 0.0661$, $wR_2 = 0.1162$
R indices (all data)	$R_1 = 0.1088$, $wR_2 = 0.1496$	$R_1 = 0.1246$, $wR_2 = 0.1400$
Largest diff. peak and hole (e Å^{-3})	0.674/−0.492	0.577/−0.654

In this article, to obtain specific products, the cobalt carbonyl clusters $Co_2(CO)_6(\mu^2$-trimethylsilylacetylene) and $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) were synthesized first, then used as reaction precursors to perform cycloaddition with diferrocenylacetylene and ferrocenylacetylene, respectively. The molar ratio of $Co_2(CO)_6(\mu^2$-trimethylsilylacetylene) and diferrocenylacetylene was controlled strictly in a 1 : 2 ratio and so was the molar ratio of $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) and ferrocenylacetylene. Only the 1,2,4,5-substituted benzenes were obtained and 1,2,3,4-substituted and 1,2,3,5-substituted benzenes were not found in reactions of **2**. This may be ascribed to steric hindrance. The reactions carried out in this work are illustrated in scheme 2.

3.2. *Characterization of 1 and 2*

Compounds **1** and **2** were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and MS (corresponding data listed in the section 2). The molecular structures are

Table 2. Selected bond lengths (Å) and torsion angles (°) of **1** and **2**.

1				**2**			
C1–C2	1.432(7)	C2–C3	1.415(6)	C1–C4	1.416(6)	C4–$C8^3$	1.395(6)
C3–C4	1.433(7)	C4–C5	1.399(6)	$C8^3$–$C1^3$	1.371(7)	$C1^3$–$C4^3$	1.416(6)
C5–C6	1.405(7)	C6–C1	1.393(7)	$C4^3$–C8	1.395(6)	C8–C1	1.371(7)
C2–C7	1.491(7)	C3–C17	1.491(7)	C4–C7	1.476(7)	C1–C6	1.491(6)
C4–C27	1.485(6)	C5–C37	1.492(6)	$C4^3$–$C7^3$	1.476(7)	$C1^3$–$C6^3$	1.491(6)
C1–C2–C3–C4		−26.7(8)		C8–C1–C4–$C8^3$		1.0(8)	
C2–C3–C4–C5		28.4(3)		C1–C4–$C8^3$–$C1^3$		1.1(3)	
C3–C4–C5–C6		−10.9(7)		$C4^3$–C8–C1–C4		1.1(6)	
C4–C5–C6–C1		−8.1(9)		$C8^3$–$C1^3$–$C4^3$–C8		1.0(8)	
C5–C6–C1–C2		9.8(0)		$C1^3$–$C4^3$–C8–C1		1.1(3)	
C6–C1–C2–C3		7.8(6)		C4–$C8^3$–$C1^3$–$C4^3$		1.1(6)	

determined by X-ray single-crystal diffraction, crystal data and relevant structural parameters are enumerated in table 1, and selected bond lengths and torsion angles are listed in table 2.

Figure 1 shows the molecular structure of **1**. Compound **1** crystallizes in the orthorhombic space group *Pbca*. Although the bond lengths (1.393(7)–1.433(7) Å) and bond angles (116.6(4)°–124.3(5)°) of a central phenyl ring have no significant deviation compared to a normal phenyl ring, the six carbons are not co-planar due to the large steric hindrance. The central phenyl ring adopts a twist-boat configuration with torsion angles of −26.7(8)° ($C_1-C_2-C_3-C_4$) and 28.4(3)° ($C_2-C_3-C_4-C_5$) (figure 1). The central phenyl ring is partially deformed and the aromatic character of the normal phenyl ring is lost. The length from Fe to Cp ring plane is from 1.636 to 1.654 Å, no significant difference. The dihedral angles of two Cp ring planes in each ferrocenyl are 2.7°, 1.9°, 2.4°, and 4.4°. Four ferrocenyl groups are attached to the central phenyl ring at the 2, 3, 4, 5 positions with bond lengths of 1.491(7) Å (C_2-C_7), 1.491(7) Å (C_3-C_{17}), 1.485(6) Å (C_4-C_{27}), and 1.492(6) Å (C_5-C_{37}), respectively. Four ferrocenyl groups attached to the central phenyl ring adopt an approximate up-down-up-down fashion. The distances of Fe3−Fe2, Fe2−Fe1, and Fe1−Fe4 are 6.490, 6.148, and 5.743 Å, respectively (figure 2).

The molecular structure of **2** is described in figure 3. Compound **2** crystallizes in a centrosymmetric structure and in the monoclinic space group *P2(1)/c*. The length from Fe to Cp ring plane is 1.642–1.652 Å, no significant difference. The dihedral angles of two Cp ring planes in each ferrocenyl are 2.8°, 5.4°, 2.8°, and 5.4°. The bond lengths and angles of

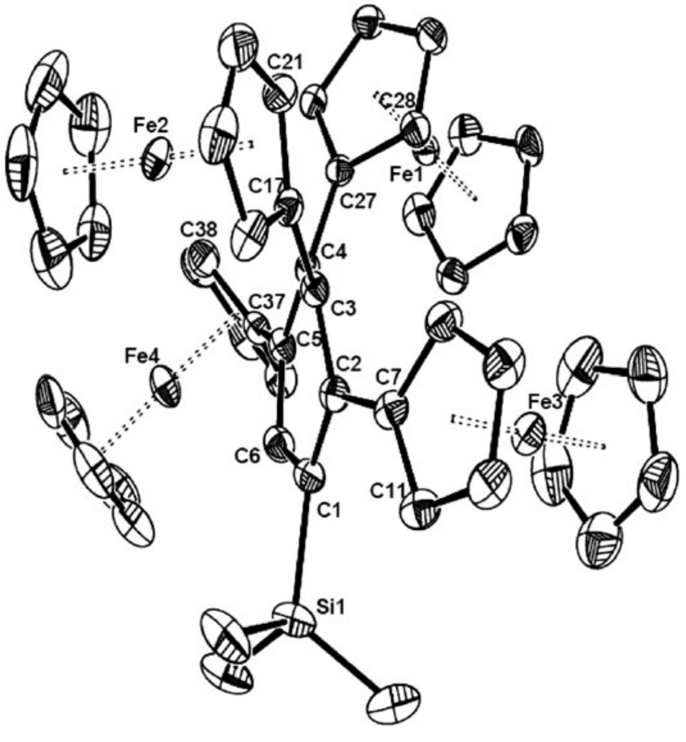


Figure 1. The molecular structure of **1**.

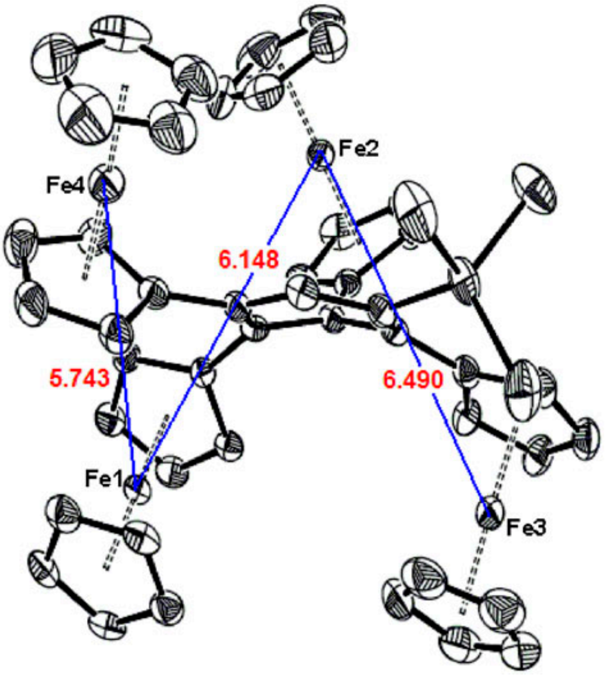


Figure 2. The molecular geometry of **1**.

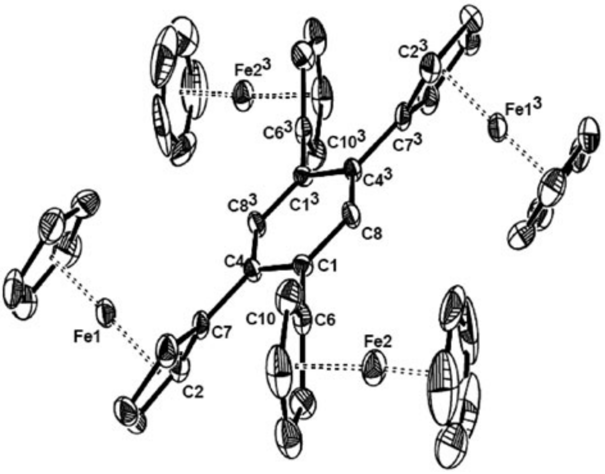


Figure 3. The molecular structure of **2**.

the central phenyl ring range from 1.371(7) to 1.416(6) Å and 116.8(4) to 123.7(5)°, respectively, with maximum torsion angle of 1.1(6)° ($C_4{}^3$–C_8–C_1–C_4 and C_4–C_8^3–C_1^3–C_4^3). This shows that the six carbons of the central phenyl ring are approximately co-planar (figure 3). Four ferrocenyl groups are attached to the central phenyl ring at the 1, 2, 4, 5 positions with bond lengths of 1.491(6) Å (C_1−C_6), 1.476(7) Å (C_4−C_7), 1.491(6) Å (C_1^3−C_6^3), and 1.476 (7) Å (C_4^3−C_7^3), respectively. The distances of Fe1−Fe2, Fe1^3−Fe2^3, Fe1−Fe2^3, and Fe2−Fe1^3 are 6.624, 6.624, 6.345, and 6.345 Å, respectively. Four iron centers are in the same plane (figure 4). Four Cp planes attached to the central phenyl ring are arranged in an approximately face-to-face fashion, the dihedral angles of which are 67.8°, 41.1°, 67.8°, and 41.1°, respectively.

3.3. *Electrochemistry*

CV and SWV were performed on a CHI 760C electrochemical analyzer using a platinum disk of radius 0.8 mm as working electrode. The electrode surface was polished with 0.05 μm alumina before each run. The reference electrode was an Ag|AgCl electrode and the auxiliary electrode was a coiled platinum wire. The supporting electrolyte used in all electrochemical experiments was tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) at 0.5 M in the mixture of acetonitrile and dichloromethane (1 : 1, V : V). We employed argon as purge gas to eliminate oxygen and nitrogen from the one-compartment cell before the electrochemical experiments.

The redox properties of **1** and **2** were studied by CV and SWV. Both compounds display three redox waves from 0 to 1.2 V (figure 5), which are assigned to the two Fe^{II}/Fe^{III} redox couples. The electrochemical data are summarized in table 3. Compound **1** displays two one-electron processes at 410 and 583 mV and one two-electron process at 739 mV. Compound **2** displays two one-electron processes at 476 and 570 mV and one two-electron process at 672 mV. From the I_{pa}/I_{pc} (≈1) values of each couple, the redox processes were chemically reversible [25–27].

The first oxidation potential of **1** (410 mV) is lower than **2** (476 mV), illustrating that trimethylsilyl has stronger electron-donating effects [28, 29]. The electronic communication effect of **1** and **2** was discussed through comparing the half-wave potential differences

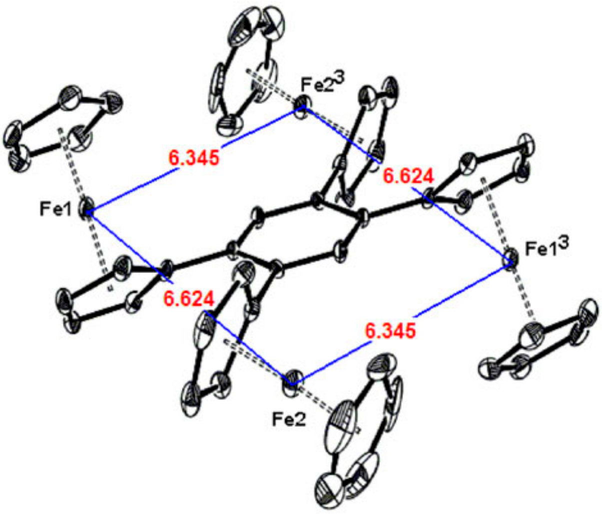


Figure 4. The molecular geometry of **2**.

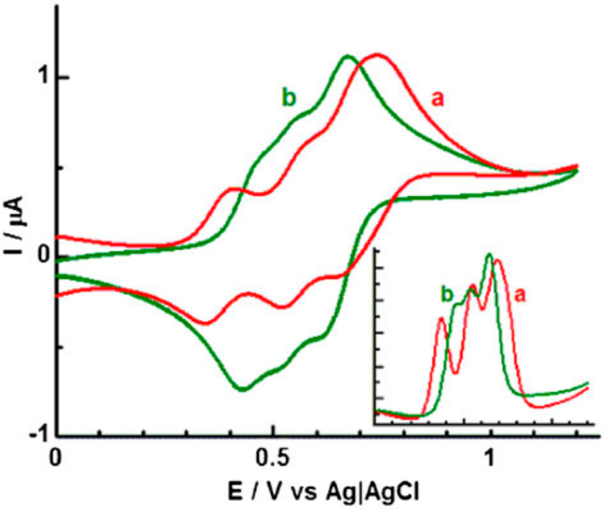


Figure 5. The electrochemical curves of **1** (a) and **2** (b).

($\Delta E_{1/2}$) between ferrocenyl units. The half-wave potential differences of the neighboring two redox couples ($\Delta E_{1/2}$) in **2** of 91 and 96 mV are lower than those in **1** of 176 and 144 mV, which indicates weaker electronic interaction among the ferrocenyl moieties in **2**. This is due to its increased spatial distance (figure 4) of the "Fe" center in neighboring ferrocenyl units. This result is consistent with the literature reported [30–34].

The ΔE values are also affected by π-conjugation, as investigated by the torsion angles of **1** and **2** (table 3). The torsion angle [C1–C2–C7–C11 (−11.80°), C4–C3–C17–C21 (−21.60°), C3–C4–C27–C28 (38.82°), and C4–C5–C37–C38 (−47.48°)] of **1** is also smaller than [C8^3–C4–C7–C2 (41.12°), C8–C1–C6–C10 (74.29°), C8–C4^3–C7^3–C2^3 (41.12°), and C8^3–C1^3–C6^3–C10^3 (74.29°)] of **2**, showing that cyclopentadienyl ring had stronger conjugation with the central phenyl ring in **1** than **2**. Hence, the total conjugation of **1** is stronger than **2**, suggesting a stronger degree of electronic interaction between ferrocenyl units in **1**; therefore, stronger electronic communication exists in **1** ($\Delta E^1_{1/2} = 176$ mV, $\Delta E^2_{1/2} = 144$ mV) than **2** ($\Delta E^1_{1/2} = 91$ mV, $\Delta E^2_{1/2} = 96$ mV). This result is consistent with our previous work [29].

3.4. *UV–visible spectroscopy*

UV–vis absorption spectra of the two compounds were recorded on a UV751GD UV–visible spectrophotometer. The compounds were dissolved in chloroform (0.1 mM) and transferred to 10 mm path length quartz cuvettes. UV–visible absorption spectra of **1** and **2** are shown in figure 6. Both showed a more intense absorption in the UV region which can be investigated for possible applications in optical recording materials. The absorption spectra of **1** and **2** show three distinct bands: a shoulder at 280 nm, a shoulder at 350 nm, and a much weaker peak at 450 nm. Obviously, the peak at 280 nm is attributed to benzene ring absorption and the one at 450 nm is assigned to the characteristic d–d transition of the ferrocene nucleus [35–37]. The shoulder peak at 350 nm is thought to be related to the cyclopentadienyl rings in the ferrocenyl molecules [35, 36]. Compound **1** is more redshifted than **2** due to its stronger total conjugation.

Table 3. The electrochemical data of **1** and **2**.

Compounds	E_{pa1} (mV)	E_{pc1} (mV)	$E^1_{1/2}$ (mV)	E_{pa2} (mV)	E_{pc2} (mV)	$E^2_{1/2}$ (mV)	E_{pa3} (mV)	E_{pc3} (mV)	$E^3_{1/2}$ (mV)	$\Delta E^1_{1/2}$ (mV)	$\Delta E^2_{1/2}$ (mV)	I_{pa1}/I_{pc1}	I_{pa2}/I_{pc2}	I_{pa3}/I_{pc3}
1	410	342	376	583	521	552	739	653	696	176	144	1.03	0.98	1.05
2	476	424	450	570	512	541	672	602	637	91	96	0.98	1.02	1.03

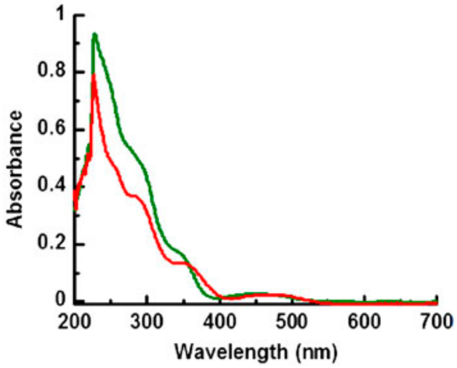
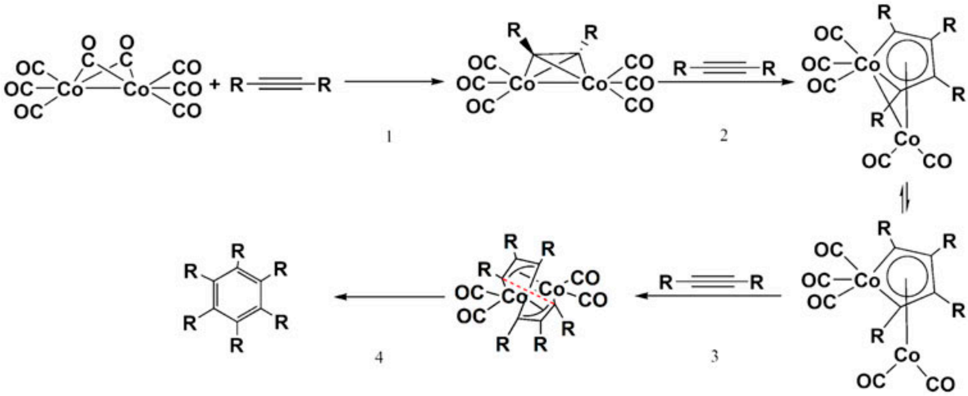
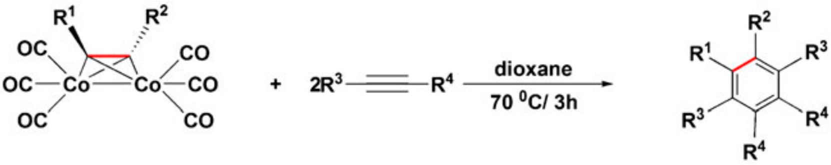


Figure 6. The absorption spectrum of **1** (red line) and **2** (green line) (see http://dx.doi.org/10.1080/00958972.2014.997720 for color version).



Scheme 1. The mechanism of $Co_2(CO)_8$-catalyzed cycloaddition of alkynes.



Scheme 2. The synthesis of **1** and **2**.

4. Conclusion

1-Trimethylsilyl-2,3,4,5-tetraferrocenylbenzene (**1**) and 1,2,4,5-tetraferrocenylbenzene (**2**) were obtained by cycloaddition reactions with $Co_2(CO)_6(\mu^2$-trimethylsilylacetylene) and $Co_2(CO)_6(\mu^2$-diferrocenylacetylene as precursors, respectively. The molecular structures of **1** and **2** were identified by single-crystal X-ray diffractions. In **1**, the central phenyl ring adopts a twist-chair configuration due to the four ferrocenyls adjacent to each other. This does not appear in **2** due to its four ferrocenyls being more decentralized. The redox properties were studied by CV and SWV. Both **1** and **2** display two one-electron processes and one two-electron process. In addition, both compounds showed good spectral properties.

Supplementary material

Crystallographic data for structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC Nos. 817282 and 816925 for **1** and **2**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223 336033.

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