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Mongin

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From ferrocene to 1,2,3,4,5-pentafluoroferrrocene: halogen effect on the properties of metallocene

William Erb,^{*a} Nicolas Richy,^a Jean-Pierre Hurvois,^{*a} Paul J. Low^{*b} and Florence Mongin^a

The sequentially fluorinated ferrocenes (1-, 1,2-di-, 1,2,3-tri-, 1,2,3,4-tetra- and 1,2,3,4,5-pentafluoroferrrocene) have been synthesized from ferrocene. Rather than a ‘perfluoro’ effect, experimental and computational analysis of the complete series robustly demonstrates a linear additive effect of fluorine on the electrochemical and spectroscopic properties of ferrocene.

Introduction

Fluorine has long been known as an important element to tune the chemical and physical properties of molecules, and has, for example, been used in fundamental studies concerning aromaticity,^{1, 2} and control of molecular electronic structures,³⁻⁵ and conformation.^{6, 7} From these fundamental aspects, fluorine and fluorinated groups are critical for applications in material science,⁸⁻¹⁰ development of drugs and agrochemicals¹¹⁻¹³ and medical diagnosis.^{14, 15} In organometallic and coordination chemistry, the combination of small size, σ -electron withdrawing and π -electron donating properties of fluorine has been used to finely tune the electronic characteristics of ligands and hence the properties of the resulting metal complexes.¹⁶⁻¹⁸

Despite these interests and the role of metallocenes in many of these areas of fundamental and applied interest, few polyfluorometallocenes have been described, and structure-property relationships are limited in scope.¹⁹⁻²¹ Concerning η^6 -coordination compounds, a few arene-vanadium,²² -chromium²³⁻²⁸ and -rhodium^{29, 30} complexes with up to six fluorine atoms on the aromatic ring have been reported. However, η^5 -coordination complexes are limited to a handful of examples (Figure 1). The first member of this family, pentafluororuthenocene $\text{Ru}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}^*$, was prepared by flash vacuum pyrolysis in 1992,³¹ and followed a few years later by a set of partially fluorinated ruthenocenes.³² Although the latter were used to prove the additive effect of fluorines on the ionization energy,³³ most of the studies were focused on the properties of $\text{Ru}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}^*$.³⁴⁻³⁷ Di- and trifluorocymanthrene derivatives³⁸ have also been prepared, and isolated in pure form in small amount for crystallographic studies,³⁹ whilst synthetic routes to 1,2-difluoroferrrocene have also been developed.⁴⁰ The first polyfluoroferrrocene was prepared by Sünkel in 2015 from fluoroferrrocene by iterative deprotometalation-NFSI (N-fluorobenzenesulfonimide) electrophilic trapping.⁴¹ However, while a sample of $\text{Fe}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}$ was isolated in pure form and crystallographically characterized, all partially fluorinated intermediates were obtained as mixtures. The same year, Metzler-Nolte and Long independently reported the synthesis of 1,1'-difluoroferrrocene, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{F})_2$, with electrochemical studies highlighting the additive effect of the two fluorines on the metallocene redox potential.^{42, 43} However, this additive relationship observed for the simple 1,1'-difluoroferrrocene is

in stark contrast to anomalously low oxidation potential reported for $\text{Fe}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}$ (+0.01 V vs. FcH/FcH^+), which was attributed to a large ‘perfluoro effect’.⁴¹

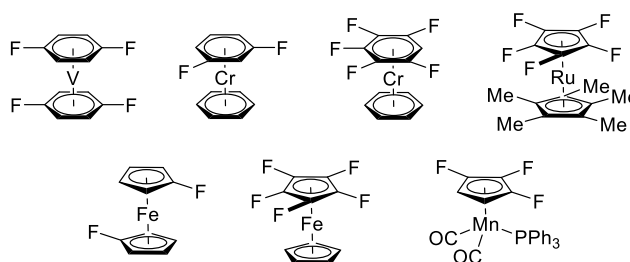


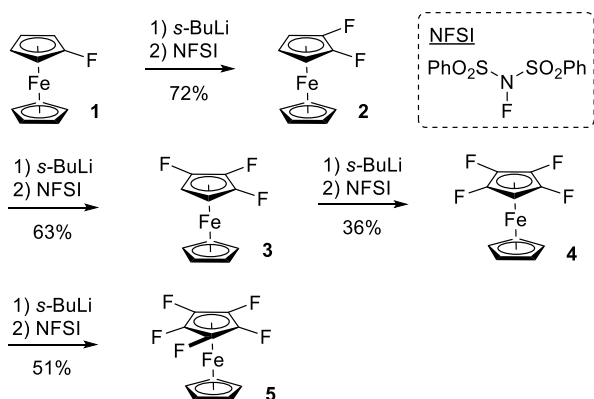
Figure 1. Selected examples of polyfluorometallocenes.

Results and discussion

To initially benchmark the effects of polyfluorination on the physical properties of ferrocene, the redox potentials of fluoroferrocene (**1**; +0.13 V), 1,2-difluoroferrrocene (**2**; +0.26 V), 1,2,3-trifluoroferrrocene (**3**; +0.42 V), 1,2,3,4-tetrafluoroferrrocene (**4**; +0.60 V) and 1,2,3,4,5-pentafluoroferrrocene (**5**; +0.76 V), relative to the FcH/FcH^+ couple were calculated ($\omega\text{B97X-D}/\text{SDD}(\text{Fe})/6\text{-31G}^{**}(\text{C}, \text{H}, \text{F})/\text{IEFPCM}(\text{SMD})\text{-CH}_2\text{Cl}_2$).^{44, 45} An almost linear increase in redox potential of the metallocenes $\text{Fe}(\eta^5\text{-C}_5\text{H}_{5-n}\text{F}_n)\text{Cp}$ with increasing fluorine substitution (i.e. n) is clear from these data. The redox potential calculated in this manner for $\text{Fe}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}$ (**5**) is also close to those of other perhalogenated metallocenes such as $\text{Fe}(\eta^5\text{-C}_5\text{Cl}_5)\text{Cp}$ (+0.77 V)⁴⁶ and $\text{Ru}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}^*$ (+1.07 V),³⁴ but clearly differs from the reported value.⁴¹ To conclusively resolve the issues, the complete series of complexes $\text{Fe}(\eta^5\text{-C}_5\text{H}_{5-n}\text{F}_n)\text{Cp}$ (**1-5**) were prepared.

As indicated above, the use of hindered lithium amide to deprotometalate fluoroferrocene prior to trapping with NFSI leads to mixtures of polyfluoroferrrocenes.⁴¹ Whilst not fully selective, cleaner functionalization of fluorinated ferrocenes can be achieved with *sec*-butyllithium (*s*-BuLi).⁴⁰ Thus, treatment of fluoroferrocene with *s*-BuLi (1.2 equiv) in tetrahydrofuran (THF) at -80 °C for 1 h before trapping the lithiated intermediate with NFSI gave a 1:9 mixture of **1** and **2** from which 1,2-difluoroferrrocene (**2**) was isolated in 72% yield after oxidative purification using FeCl_3 (1.2 M aqueous solution) (Scheme 1).^{43, 47, 48} Further deprotonation of **2** and trapping gave

a mixture of di-, tri- and tetrafluoroferrrocenes in a ~1:8:1 ratio. 1,2-Difluoroferrrocene (**2**) was removed from the product mixture by oxidative purification (3 M aqueous solution of FeCl₃) with compounds **3** and **4** subsequently separated by column chromatography (63 and 5% yields, respectively). When 1,2,3-trifluoroferrrocene (**3**) was engaged into another deprotonation-trapping sequence, a crude mixture of **3**, **4** and **5** (~2:7:1) was obtained from which the three compounds were isolated in 10, 36 and 4% yields, respectively, by column chromatography. A final deprotonation-NFSI trapping sequence from **4** led to 1,2,3,4,5-pentafluoroferrrocene (**5**), isolated in 51% yield (10% of recovered **4**). Across the sequence of reactions, the formation of the various by-products might take place in the course of the trapping step due to the moderate electrophilicity of NFSI and the higher acidity of the formed fluoro product.⁴⁹⁻⁵¹



Scheme 2. Synthesis of fluoroferrocenes **1-5**.

The redox behavior of fluoroferrocenes **1-5** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dry, oxygen-free dichloromethane or acetonitrile, at a concentration of 1 mM with *n*Bu₄NPF₆ (0.1 M) as the supporting electrolyte (Table 1). All measurements employed a glassy carbon disk working electrode, an Ag/AgCl reference electrode and a glassy carbon rod counter electrode.

In dichloromethane, each of the (poly)fluoroferrocenes **1-5** exhibited a reversible, one-electron oxidation process at a scan rate of 100 mV·s⁻¹ (Figure 2). However, in acetonitrile, the tetra- and pentafluoroferrocenes **4** and **5** underwent an irreversible oxidation process (Figure 3). Similar behavior was reported for Ru(η⁵-C₅F₅)Cp³⁴ and Fe(C₅Cl₅)Cp⁴⁶ for which reversibility improves at very high scan rates. The oxidation of **5** in dichloromethane becomes irreversible upon introduction of acetonitrile. This observation indicates a solvent-dependent decomposition pathway, in which the modestly nucleophilic acetonitrile reacts with the highly electrophilic polyfluoroferrocene cation, explaining the loss of reversibility in this solvent.^{52, 53}

Table 1 Electrochemical data (in V).^[a]

Compd	$E_{pa}^{[b,c]}$	$E_{pc}^{[b,c]}$	$i_{pa}/i_{pc}^{[b,c]}$	$E_{1/2}^{[c,d]}$	$E_{1/2}^{[d,e]}$	$\Delta E^{[f]}$
1	0.18	0.07	0.99	0.14	0.12	0.13
2	0.33	0.22	0.95	0.28	0.26	0.26
3	0.47	0.36	1.00	0.42	0.42	0.41
4	0.68	0.57	0.97	0.62	0.56	0.59
5	0.86	0.75	1.00	0.82	0.75	0.76

[a] Potentials values given relative to FcH/FcH⁺, scan rate = 100 mV·s⁻¹. [b] From CV experiments. [c] In CH₂Cl₂. [d] From DPV experiments. [e] In MeCN. [f] From computations.

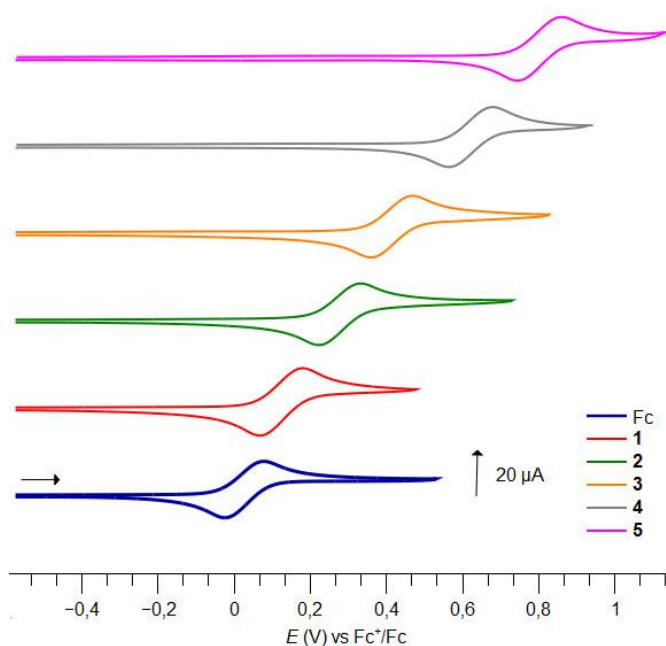


Figure 2. Superposition of CV voltammograms of ferrocene and its fluorinated derivatives **1-5** in CH₂Cl₂.

The redox potentials of the 1,1'- and 1,2-isomers of difluoroferrrocene, 1,1'-difluoroferrrocene ($E_{1/2} = 0.24$ V)⁴³ and 1,2-difluoroferrrocene (**2**; $E_{1/2} = 0.29$ V) are similar. Therefore, at least for light halogens, whether the two substituents are on the same Cp ring or distributed over both rings have comparable effects on the redox potential. The successive introduction of fluorine atoms to a Cp ring leads to a gradual increase (+0.16 V per fluorine) in the experimentally determined redox potential (Figure 2), in a manner entirely consistent with the calculated values. From both CV and DPV experiments, the $E_{1/2}$ and E_p values obtained for **5** are close to that predicted by the computational model (0.76 V). As commonly observed for other substituted ferrocenes,^{43, 54-57} a linear relationship exists between the redox potential of the organometallic and the sum of Hammett constant σ_p ⁵⁸ according to the equation $E_{1/2} = 2.0791 \sum \sigma_p - 0.92$ ($R^2 = 0.9924$; plot S11).

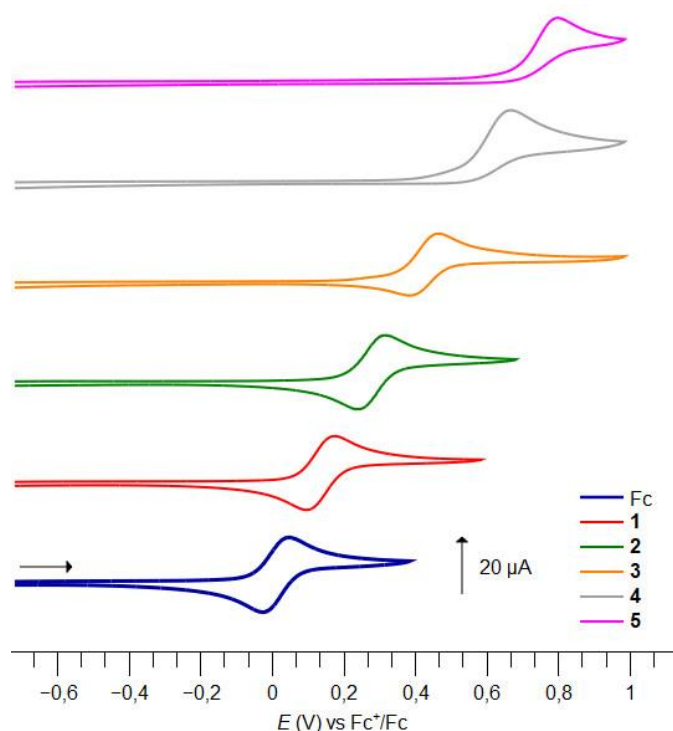


Figure 3. Superposition of CV voltammograms of ferrocene and its fluorinated derivatives **1-5** in CH₃CN.

Although fluorine is the most electronegative element, its inductive effect is counter-balanced by a strong resonance effect resulting from an overlapping of the fluorine lone pair with the Cp π orbitals.^{36, 42} As a result, Long has articulated a correlation between $E_{1/2}$ and the resonance effect parameter (R).⁴³ Here, the redox potentials of the (poly)fluoroferrocenes **1-5** are plotted against the sum of R to give a linear relationship $E_{1/2} = -0.4161 \sum R - 0.0244$ ($R^2 = 0.9924$) (Figure 4). A similar analysis of the available electrochemical data from (poly)chloroferrocenes $\text{Fe}(\eta^5\text{-C}_5\text{H}_{5-n}\text{Cl}_n)\text{Cp}$ ($n = 0, 1, 2, 5$),⁴⁶ gives $E_{1/2} = -0.6878 \sum R - 0.0249$ ($R^2 = 0.9924$), from which the redox potential of 1,2,3,4-tetrachloroferrocene is estimated ~ 0.55 V, in good agreement with the $E_{1/2}$ value of 1,1',2,2'-tetrachloroferrocene (0.51 V vs. FcH/FcH^+).⁵⁷ These simple linear equations therefore allow a reasonable prediction of the redox potential of ferrocenes bearing light halogens (F, Cl).

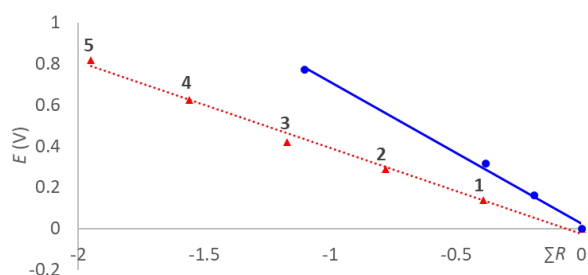


Figure 4. $E_{1/2}$ values plotted against the sum of R values for fluoroferrocenes **1-5** (red triangle, dotted line) and chloroferrocenes (blue circles, solid line).

Plots of the available $E_{1/2}$ vs. $\sum R$ for mono- to pentahomohalogenoferrocenes are given the SI.^{43, 57} The data show that the redox potential of the four (F, Cl, Br, I) mono-, the four 1,1'-homodihalogenoferrocenes fall into distinct clusters, and two pentahalogenoferrocenes $\text{Fe}(\eta^5\text{-C}_5\text{Cl}_5)\text{Cp}$ and $\text{Fe}(\eta^5\text{-C}_5\text{F}_5)\text{Cp}$ fall into a third one (Plot SI2). As discussed by Long, the data within each cluster are non-linear with electronegativity of the halogen, but reflect more subtle combination of factors including orbital re-ordering, changes in hybridization and frontier orbital composition, electrostatic repulsion between metal and Cp ring orbitals as well as through-space interactions between the iron center and halogen atoms.⁴³ The redox potential of the three 1,1',2,2'-tetrahalogenoferrocenes (Cl, Br, I) recently reported by Butler are lower than expected by adding the effects of the substituents and closer to that of 1,2,3-trifluoroferrocene than to 1,2,3,4-tetrafluoroferrocene. Therefore, summing the individual contributions of adjacent substituents, which seems to apply for fluorine, might be questioned for heavier halogens, especially bromine and iodine, and reinforces the multi-parameter considerations of Long in rationalizing the substituent effects of the heavier halogens.

The UV-visible absorption spectra of ferrocene and fluoroferrocenes **1-5** were recorded in dichloromethane (Figure 5). Ferrocene exhibits an absorption band at 441 nm, resulting from the unresolved $^1A_{1g} \rightarrow ^1E_{1g}$ and $^1A_{1g} \rightarrow ^1E_{2g}$ spin-allowed d-d transition, which is responsible for the orange color of this compound, with a low molar extinction coefficient ($\epsilon = 94 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).^{59, 60} It was previously shown that the introduction of one or two fluorines resulted in a hypsochromic shift of this band (Table 2, Figure 5).⁴³ Here, a similar effect was observed with a regular decrease of this band wavelength upon fluorination. A similar, although smaller trend was noticed upon the introduction of methyl substituents⁵⁶ while other functional groups usually led to a bathochromic shift.⁶¹⁻⁶³ To further investigate the electronic structure of polyfluoroferrocenes, the energies of the HOMO and LUMO were calculated. As reported by Long,⁴³ fluorination mainly stabilizes the HOMO while a weak destabilization of the LUMO was noticed from 1,2,3-trifluoroferrocene (Table 2). The HOMO-LUMO gap (E_{H-L}) were also plotted against the number of fluorines (n) to give a linear relationship $E_{H-L} = 0.0954 n + 8.5948$ ($R^2 = 0.9841$; plot SI3). A similar analysis partially reveals some correlation between the absorption band wavelength and the HOMO-LUMO gap with the relationship $\lambda_{\text{max}} = -93.928 E_{H-L} + 1250.2$ ($R^2 = 0.9452$; plot SI4).

Table 2 UV-vis spectroscopic data in CH₂Cl₂ and energy levels.

Compd	λ_{max} (nm)	ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{H-L} (eV)
Ferrocene	441	94	-7.72	+0.86	8.58
1	435	109	-7.82	+0.86	8.68
2	427	119	-7.94	+0.86	8.80
3	418	132	-8.06	+0.85	8.91
4	407	135	-8.19	+0.80	8.99
5	395	145	-8.34	+0.70	9.04

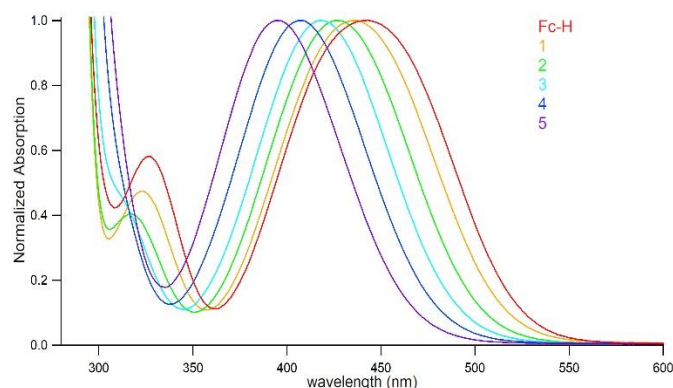


Figure 5. Normalized UV-vis spectra of ferrocene and compounds **1-5** in CH_2Cl_2 .

There are further correlations between the degree of fluorination and the ^1H and ^{13}C NMR chemical shifts of the Cp rings in **1-5**. While estimates of the ^1H shifts from the sum of individual substituent effects have been made for 1,1'- and 1,2-disubstituted ferrocenes,⁶⁴ such additive relationships have not been explored for more highly substituted derivatives. Here, data obtained from the detailed characterization of compounds **1-5** allowed the calculations of chemical shift increments ($\Delta\delta$) arising from the introduction of fluorine (see SI). For ^1H shifts (Figures 6 and 7, Table SI1), the deshielding effect of fluorine on the α position (next to the last introduced fluorine) increased with the number of fluorines while the opposite effect (decrease of shielding) was observed on the β position (remote from the last introduced fluorine). The chemical shift of the protons of the unsubstituted Cp ring are essentially independent of the degree of fluorination. Concerning ^{13}C shifts (Figures 6 and 8, Table SI2), increasing fluorination results in a decrease of shielding of α and β positions but little deshielding of both the C_{ipso} and the unsubstituted Cp ring. Therefore, with more than two fluorines on the same ring, our new increments, specific to polyfluoroferrrocenes, need to be used for accurate chemical shifts predictions of polyfluoroferrrocenes substituted with other functional groups.

The ^{19}F NMR spectra were similarly analyzed to evaluate the effect of additional fluorines on the chemical shift of fluoroferrrocenes. While a single fluorine on ferrocene displays a resonance at -189 ppm, two adjacent fluorine atoms have a chemical shift between -202 and -210 ppm and a fluorine surrounded by two others has a shift comprised between -214 and -217 ppm. Close chemical shifts values were reported by Hughes for polyfluororuthenocenes.³² Therefore, in average, the introduction of a fluorine atom upfields the chemical shift of the fluorine already present by 12.5 and 3.7 ppm at the α and β positions, respectively.

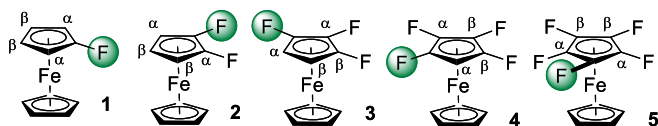


Figure 6. α and β positions based on the last fluorine atom introduced.

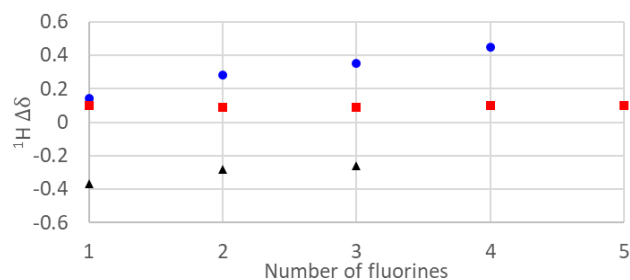


Figure 7. ^1H $\Delta\delta$ (ppm) against number of fluorines: α position (blue circles), β position (black triangles) and Cp (red squares).

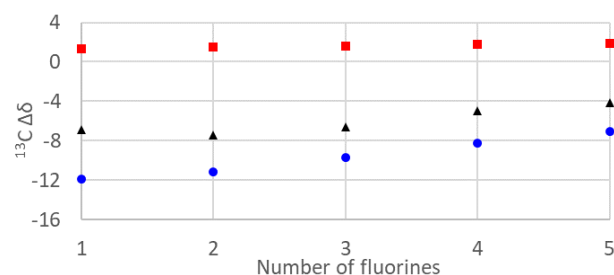


Figure 8. ^{13}C $\Delta\delta$ (ppm) against number of fluorines: α position (blue circles), β position (black triangles) and Cp (red squares).

Conclusions

In conclusion, an improved synthesis of 1,2,3,4,5-pentafluoroferrrocene together with each of the partially fluorinated derivatives has been reported. Experimental data and computational estimates are consistent with an approximately linear, additive effect of fluorine on the redox potentials of ferrocenes. UV-visible spectra reveal a regular hypsochromic shift of the lowest energy ferrocene absorption band upon addition of fluorine atoms, which correlates with the increasing HOMO-LUMO gap from ferrocene to 1,2,3,4,5-pentafluoroferrrocene. Finally, a new set of NMR chemical shifts increments specific for polyfluoroferrrocenes are reported. Taking together, these results give the first general overview of polyfluoroferrrocenes and can be used to design derivatives with specific properties.

Author Contributions

W.E. performed the synthesis of the fluoroferrrocenes, performed the UV-visible experiments with N.R. and the electrochemical study with J.-P.H. P.J.L. performed the calculations. All co-authors participated in scientific discussions and equally contributed to manuscript writing.

Conflicts of interest

There are no conflicts to declare.

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