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# Electronic structure and near-IR transitions of FcC<sub>2</sub>R and FcC<sub>4</sub>R dyads

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#### Abstract

This paper describes the orbital configuration which provides a basis for the understanding of the electronic structure and spectroscopic properties of 17e and 18e FcC<sub>2</sub>R and FcC<sub>4</sub>R dyads, where R is H, 1-naphthyl, 9-anthryl, 3-pyrenyl, perylenyl. DFT calculations show that destabilisation of the ferrocenyl  $\pi$  orbitals upon binding a C=CR group to a Cp ring leads to the metal-based a<sub>1</sub> orbital dropping below the e<sub>1</sub>-a so that the frontier orbital configuration is (e'<sub>2</sub>-a, $\pi$ )<sup>2</sup>(e'<sub>2</sub>-b, metal)<sup>2</sup>(e'<sub>1</sub>-a, $\pi$ )<sup>2</sup>, (a<sub>1</sub>, metal)<sup>2</sup>. The contribution of the aryl group to the  $\pi$  e<sub>2</sub>-a and e<sub>1</sub>-a orbitals varies with the annelation of the ring. The LUMO is aryl based. The calculations are consistent with the spectroscopic data for the 18e species. Oxidation to the 17e cations does not change the orbital configuration but the orbital energies are lowered by the positive charge centred on the Fe. A strongly solvatochromic transition in the near-IR, a signature for the 17e cations, is best described as an LMCT transition but the contribution of C<sub>2</sub>R and C<sub>4</sub>R to the donor and acceptor levels depends on the ionization energy of the aryl  $\pi$  orbital. LMCT energies decrease from FcC<sub>2</sub>R to FcC<sub>4</sub>R dyads. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Electronic structure; DFT calculations; Ferrocenylaryl dyads; Ferroceniumaryl dyads; NIR spectra

## 1. Introduction

Many aspects of the electronic structure of closed shell metallocenes, especially ferrocene [1–5], have been investigated, both theoretically and experimentally. With the current focus on ferrocenyl materials with second-order NLO properties [6,7], these studies have extended into ferrocenyl derivatives where electron acceptors are bound to one or two cyclopentadienyl rings, especially via a  $\pi$ -linkage [2,8–10]. A detailed description of the electronic structure for this class of compound has evolved, the salient features being an understanding of the ferrocenyl-( $\pi$ -link)-acceptor energy levels and consequential optical transitions. The electronic structure of compounds with strong donors on a Cp ring [11] or dyads with a ferrocenyl-( $\pi$ -link)-donor

motif [12] have not received the same attention. Barlow and Marder [2] have commented that a  $D_{5h/5d}$  metallocene can interact with a  $\pi$ -bridge both via a cyclopentadienyl ring and through a metal-based orbital when an organic acceptor was involved. Whether this situation also pertains in electron-rich  $\pi$ -linked dyads, and/or with ferrocenium analogues, is the thrust of this paper. This was of interest to us as any change in the electronic structure, either in the neutral or oxidized molecule, may enable the classical quenching effect of the metallocene to be modified if a fluorophore is bound to a cyclopentadienyl ring via a  $\pi$ -conjugated bridge. This has been achieved where the fluorophore is a strong electron acceptor [13–15].

In a previous paper [16] we reported the synthesis and molecular structure of the ferrocenyl dyads 1a-f and 2a-f and [FcC=C-C=CR]. Spectroscopic and structural data indicated that there was little mutual perturbation of the Fc and aryl groups via the unsaturated link in the ground

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state of the dyad. But this was not true when the ferrocenyl group was oxidized to the ferrocenium analogue. Absorption bands in the 400–700 nm region of the visible spectrum were not typical of ferrocenium compounds and all oxidized dvads had weak bands in the near-IR. Similar NIR bands have been reported for a number of ferrocenium derivatives [10,11,17] and the effects of donors on the ferrocenium LMCT band have been documented [17]. We subsequently found that these near-IR bands were also a feature of dyads with  $FcC \equiv C$ - or FcC = C-group, even when R was a strong acceptor (e.g. naphthalimide [16]). They were also observed in oxidized dyads of general type,  $Mc^+-C \equiv C-R$  or  $Mc^+ C \equiv C - R$ , where Mc is a donor metallocene fragment such as the isolobal  $\eta$ -C<sub>5</sub>H<sub>4</sub>Co(Ph<sub>4</sub>C<sub>4</sub>). In order to gain an insight into the origin of the NIR bands, DFT calculations were performed on the dyads 1a-f [18] and 2a-f. The  $\pi$  link between the ferrocenyl and aryl groups significantly perturbs the ferrocenyl energy levels leading to a different orbital configuration to that of ferrocene. This one-electron configuration provides an explanation of the interesting spectroscopic properties and electrochromism displayed by these dyads



## 2. Results and discussion

#### 2.1. DFT calculations on 18e dyads

Density functional theory (DFT), which is wellperformed for ferrocene [4,5] and derivatives [9b], was used to probe the influence of the  $-C \equiv C$  and aryl group on the frontier orbitals of ferrocene. B3LYP calculations were carried out on **1a**-**f** and **2a**-**f**. Iso-surfaces for the frontier orbitals for **1d** are represented in Fig. 1a; surfaces for the other molecules are available from the authors. Calculated orbital energies are given in Table 1 and schematically represented in Fig. 2. B3LYP/6.31G(d) calculations of the optimised geometries were in good agreement with those found in the X-ray crystal structures [16]. An eclipsed geometry for the Cp rings was found for all dyads so the appropriate ferrocenyl point group is  $D_{5h}$  but the subgroup  $D_5$  is adequate. For the dyads the symmetry is  $C_{2v}$ .

Ferrocene ( $D_5$ ) has an  $e'_2(x^2 - y^2, xy)$  HOMO, which is predominately a  $\delta$  bond and metal in character. The  $e'_2$  lies 0.35 eV above the metal-based  $a_1(d_{z^2})$  orbital. The  $e'_1(Cp + d_{xz/yz})$  is the strongest bonding interaction. Ionization potentials for the  $e_2$ ,  $a_1$ ,  $e_1$  frontier orbitals of ferrocene are, respectively, 6.88, 7.23 and 8.72 eV [4]. The addition of a C=C to an aromatic ring raises the ioniza-

#### а



Fig. 1. (a) Frontier orbitals of 1d; (b) comparison of HOMO and HOMO - 2 frontier orbitals for 1b and 1d.

tion energy of the  $\pi$  HOMO and for HC=CR the IP's range from 9.12 eV for ethynylbenzene to 8.12 eV for the larger annelated rings [19]. Consequently, the  $\pi$  orbitals of the C=CR group are ideally placed for a strong  $\pi$  interaction with ferrocene orbitals, with the aromatic HOMO having a stronger interaction with the e<sub>2</sub> orbital as the ring size increases; this was confirmed by the B3LYP calculations (vide infra). The DFT calculations show that the introduction of a conjugated substituent does indeed have a significant impact on the relative energies of the ferrocene orbitals, particularly the strongly bonding e'\_1 level (Fig. 2).

Molecule	HOMO – 3	HOMO - 2	HOMO - 1	НОМО	LUMO
	e' <sub>1</sub>	$a'_1$	e'2	e'_	e' <sub>1</sub>
FcH	-0.2487	-0.22228	-0.18981	-0.18980	0.00784
	$e_1'$ - $a/a_1$	$e'_1 - a/a_1$	e'b	e'a	
1a 2a	-0.23194 -0.2257	-0.22827 -0.2219	-0.19687 -0.1922	$-0.19560 \\ -0.1900$	$-0.00892 \\ -0.0120$
	a <sub>1</sub>	e' <sub>1</sub> -a	e'b	e'2-a	
1b 1c 1d 1e	-0.22892 -0.22958 -0.23850 -0.22985	-0.21229 -0.20519 -0.19965 -0.19986	-0.19605 -0.19699 -0.19763 -0.19704	-0.19184 -0.19011 -0.18173 -0.18435	$\begin{array}{r} -0.03386 \\ -0.05012 \\ -0.06893 \\ -0.06393 \end{array}$
	$e'_1$	$a'_1$	e'_	$e_2'$	$e'_1$
$[FcH]^{+b}$	-0.4281(a)	-0.4281(a)	-0.3916(β)	-0.3916(β)	-0.2862(β)

Table 1			
Molecular	orbital	energies <sup>a</sup>	

<sup>a</sup> Energies in au.

<sup>b</sup> Energies are given for the  $\alpha$  or  $\beta$  one-electron orbitals.



Fig. 2. Calculated orbital energies for 18e and 17e dyads compared to ferrocene.

451

For ease of tracing the perturbation of the ferrocenyl orbitals, the dyad frontier orbitals arising from the degenerate ferrocenyl orbitals in lower symmetry will be designated as  $e'_2-a/e'_2-b$  and  $e'_1-a/e'_1-b$  rather than a formal  $C_{2v}$  designation. One of the degenerate  $e'_2$  or  $e'_1$  orbitals has the correct nodal symmetry ( $e'_2$ -a and  $e'_1$ -a) to interact with the HOMO of the C=CR substituent.

We first consider the effect of adding a -C=CH group to the Cp ring of ferrocene. The energies of both orbital pairs,  $e'_2-a/e'_2-b$  and  $e'_1-a/e'_1-b$ , are lowered relative to the parent ferrocene orbital. There is an orbital mismatch for the ferrocenyl- $\pi$ -substituent interaction (Fig. 1) and the orbital involved in the  $\pi$  interaction, the e'<sub>2</sub>-a, is slightly destabilised relative to the  $e'_2$ -b orbital which is entirely metal-based. This is the reverse of that found when the  $C_1$  substituent is an electron-withdrawing group [9b]. Similarly the strongly interacting e'<sub>1</sub>-a orbital is higher in energy than the metal-based e'1-b. This destabilisation of the  $\pi$  e'<sub>1</sub>-a orbital has an extremely important consequence for the relative energy of the  $e'_1$ -a and  $a_1$  ( $d_{z^2}$ ) orbitals. For 1a, mixing of these two orbitals occurs with the result that the one-electron HOMO - 2 and HOMO - 3 both have  $d_{z^2}$  and  $d_{xz}$  character. The orbital configuration for 1b-f is more simple. For these dyads the increase in energy of the  $\pi$  (e'<sub>1</sub>-a) orbital leads to a crossover of energy such that the HOMO – 2 orbital is now the  $e'_1$ -a combination and the HOMO - 3 the  $a_1$  (see Fig. 2). The frontier orbital configuration for **1b–f** is thus  $(e'_2-a)^2$ ,  $(e'_2-b)^2$ ,  $(a_1)^2$ ,  $(e'_1-a)^2$ ,  $(e'_1-b)^2$ (Figs. 2 and 5).

There is a progressive destabilisation of the HOMO  $e'_2$ -a  $\pi$ orbital as the annelation of the aryl ring increases. Since there is little variation in the energy of  $e'_2$ -b, the energy difference between HOMO and HOMO - 1 increases as the ionization energy of the aryl decreases, 0.035 eV (1a) to 0.43 eV (1d), although it is still relatively small. More significant is the increasing destabilisation of the strongly bonding HOMO - 2 ( $e'_1$ -a) orbital such that the HOMO - 2/ HOMO - 3 separation increases from 0.45 eV for 1a to 1.06eV for 1e; in fact, the HOMO - 1/HOMO - 2 orbitals for 1e are almost degenerate (separation 0.05 eV) (Table 1). Concomitant with the increase in energy of the HOMO, there is an increasing –C=CR contribution to the HOMO; by 1d the HOMO has a large  $-C \equiv CR$  component. This trend nicely correlates with the decreasing ionization potential of the C $\equiv$ CR group. Conversely, there is an increase in the metal character of HOMO  $- 2 (e'_1-a)$  (Fig. 1b).

Calculations on the ethenyl dyads **2a**, **2c** and **2d** indicated that the orbital configuration  $(e'_2-a,\pi)^2(e'_2-b, metal)^2-(e_1-a,\pi)^2$ ,  $(a_1, metal)^2$  also held for the ethenyl series. An ethenyl group interacts more strongly with the ferrocene moiety than an ethynyl group and this is reflected in the higher energy of the  $\pi$  orbitals for the ethenyl series. As a consequence, the HOMO for ferrocene and **2a** have almost the same energy which accounts for the observation that the potentials for the [Fc]<sup>+/0</sup> couple for ferrocene and **2a** are similar (0.55 V and 0.52 V, respectively) whereas that the ethynyl dyad **1a** is more difficult to oxidise (0.63 V). Calculations show that the LUMO in all the dyads is entirely aryl-based and this is consistent with experimental data. Their reduction potentials were similar to the free arene in the same solvent and simulation of the EPR spectra of the radical anions  $1(b-f)^{-1}$  and  $2(a-e)^{-1}$  was achieved using the values obtained from EPR spectra of the HC==CR<sup>-1</sup> and HC==CR<sup>-1</sup> radical anions.

## 3. Electronic spectra

Identification of the lowest energy bands in the UV-Vis spectra was hampered by the overlap with the very intense  $\pi - \pi^*$  transition of the aryl group. Nevertheless, the weak lowest energy band does not change significantly in energy as the annelation of the ring increases; the energies are all  $22500 \pm 200 \text{ cm}^{-1}$  compared to  $22700 \text{ cm}^{-1}$  for ferrocene. These bands can be given an assignment analogous to the lowest energy spin-allowed d-d transition  $({}^{1}A_{1} \rightarrow aE_{1})$  of ferrocene [1] and the invariant character of this transition is consistent with the relatively constant HOMO-LUMO band gap across the series. Resonance Raman spectra  $(\lambda_{\text{exc}} = 457.9 \text{ nm})$  supported this assignment for the lowenergy band as there was a weak enhancement of the  $v_{C=C}$ band, the ferrocenyl ring breathing mode at  $1100 \text{ cm}^{-1}$  and  $v_{\rm Fe-C}$  at 298 cm<sup>-1</sup> and aryl modes. As noted previously [16], the small red-shift in the  $\pi$ - $\pi$ <sup>\*</sup> transition of the C=CR group shows that there was not strong perturbation by the ferrocenvl moiety.

Electrochemical oxidation of 1a-f and 2a-f at the potential of their  $[Fc]^{+/0}$  couple generated the respective greenblue  $[1a-f]^+$  and green  $[2a-f]^+$  17e cations. The C<sub>4</sub> species,  $[Fc-(CH=CH)_2R]^+$  (R = Ph, naph, pyr, anthryl), were also produced to study the effect of extending the unsaturated link. For  $[1b-f]^+$  constant isosbestic points, complete spectral reversibility when the potential is cycled in an OTTLE experiment, and the fact that identical spectra were obtained by controlled chemical oxidation, attest to the stability of the 17e species. There was spectroscopic evidence that the lifetime of  $1a^+$  was much shorter due to decomposition to the butadiene species (FcC=C)<sub>2</sub>. Representation of the cations as  $Fc^+C \equiv CR$  in the ground state is vindicated by the vibrational data which show that shifts in the ferrocenvl vibrational bands are similar to those that occur with the formation of a ferrocenium ion [20]. For example, the Raman spectrum of  $1d^+$  shows a shift of the Fc ring-breathing mode of  $+7 \text{ cm}^{-1}$  and there is a typical  $Fc^+$  band at 1113 cm<sup>-1</sup> in the infrared spectrum.

In the ferrocenium cation [1,21-23], the <sup>2</sup>E<sub>2</sub> state is 0.46 eV more stable than <sup>2</sup>A<sub>1</sub> state and the ground state configuration is  $e_2^3 (xy, x^2 - y^2)a_1^2 (z^2)$ . Previous calculations on ferrocenium derivatives [9b], and PE data indicate that the orbital ranking does not change from that in the 18e parent. Our DFT calculations on  $[1a-b]^+$ , and preliminary results for the ethenyl series, also confirmed that the frontier orbital energy sequence was also unchanged upon oxidation,  $[(e'_2-a)^1(e'_2-b)^2(e_1-a)^2, (a_1)^2]$ , and that aryl contribution to the one-electron orbitals in the 17e and

18e species was similar. Overall, the energies of the occupied orbitals are lower than in the 18e analogues due to the coulombic effect of the positive charge. The HOMO– LUMO gap is significantly smaller than for the corresponding neutral species and it decreases from  $Fc^+$  to  $1a^+$  and as the ring size increases.

Broad  $(v_{1/2} \sim 2100 \text{ cm}^{-1})$ , weak bands ( $\varepsilon$  700– 1550 M<sup>-1</sup>cm<sup>-1</sup>), with energies from 7600 to 14300 cm<sup>-1</sup> (band **A**, Fig. 3, Table 2), were a feature of the electronic spectra of all 17e C<sub>2</sub> and C<sub>4</sub> dyads. The energies for the ethenyl compounds are red-shifted relative to the ethynyl series (Table 2) indicative of a stronger  $\pi$  interaction. Interestingly, the intensity and energy of these bands *increased* from the C<sub>2</sub> to the C<sub>4</sub> analogue; that is, with the interpolation of another -C=C group between the donor arene and acceptor (Table 2). So rather than distance reducing the increase in the energy of the e<sub>1</sub>-a orbital, it has the opposite effect, implying that longer conjugatedchain ferrocenium dyads could have significantly more intense NIR bands. The anomalous behaviour of  $2e^+$  in the trend data, discussed elsewhere [16], is probably due to steric hindrance involving the ethenyl  $\alpha$ -H atoms restricting the  $\pi$  interaction.

Support for an LMCT assignment for these NIR bands came from several sources. (1) The energy of **A** was dependent on the annelation of the aryl group (Table 2) and plots of these energies against the first vertical ionization energy of the respective aryl group are linear. The intensity also increases as the IP of the aryl group decreases. (2) A large negative solvatochromic shift  $\Delta E_{solv}$  of 900–1200 cm<sup>-1</sup> between CH<sub>2</sub>Cl<sub>2</sub> ( $\varepsilon = 9.1$ ) to MeCN ( $\varepsilon = 37.5$ ) is indicative of a larger dipole in the ground state of the cations than the excited state. This is consistent with a CT assignment as in the excited state configuration of the cations have the



Fig. 3. OTTLE spectrum of 1d, typical of the aryl dyads; 0.7 V on Pt, CH<sub>2</sub>Cl<sub>2</sub>, 293 K.

Table 2				
Representative data for LMC	T (A) and	HOMO-LUMO	(B)	transitions <sup>a</sup>

R	Fc <sup>+</sup> -C=C-R			Fc <sup>+</sup> -CH=CH-R			Fc <sup>+</sup> (CH=CH) <sub>2</sub> R	
	$\lambda_{\max}(\mathbf{A})$	ε(A)	$\lambda(\mathbf{B})$	$\lambda_{\max}(A)^{b}$	$\epsilon(\mathbf{A})$		$\lambda_{\max}(\mathbf{A})^{\mathbf{b}}$	$\epsilon(\mathbf{A})$
Н	14.3		17.2	13.9		17.1		
Phenyl	12.6	0.7	17.4	11.1	0.6	17.1	9.5	0.5
1-Naphthyl	11.5	0.8	17.1	10.5	0.7	17.2		
2-Naphthyl	11.8	0.7	17.2	10.4	1.3	17.2	9.1	0.4
Phenanthryl	11.1	0.7	17.0	10.5	1.3	17.2		
Anthryl	8.9 <sup>b</sup>	0.9	d	9.52	0.7	d	9.3	1.2
Pyrenyl	9.8°	1.3	17.5	9.0	1.6	17.5	8.3	1.9
Perylenyl	8.3	1.4	d	7.6	1.5	d		

<sup>a</sup>  $\lambda_{max}(A)$ ,  $\epsilon(A)$ ,  $\lambda_{max}(B)$ , refer to the data for bands A and B labelled in Fig. 3.  $\lambda_{max} \times 10^{-2} \text{ cm}^{-1}$ ;  $\epsilon \times 10^{-2} \text{ M}^{-1} \text{ cm}^{-1}$ . Recorded in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> In MeCN, 9.7.

<sup>c</sup> In MeCN, 10.6.

<sup>d</sup> Obscured by  $\pi$ - $\pi$ <sup>\*</sup> tail.

positive charge spread throughout the  $\pi$  system; in the ground state it is localised on the ferrocenyl acceptor. (3) For a CT transition the energy should be related to the electrochemical parameters of the donor and acceptor moieties; this is indeed the case (Fig. 4). (4) The Raman spectrum resonant with these bands shows an enhancement of modes associated with both Fc<sup>+</sup> and aryl units. The ring-breathing modes of the Fc/Fc<sup>+</sup> component show an *increase* in resonance enhancement on going from  $1b-f \rightarrow [1b-f]^+$  whereas there is a threefold *decrease* in enhancement in the equivalent modes for FcH to FcH<sup>+</sup>. These data imply that the Fc-based modes are deriving enhancement from an additional electronic transition that is not isolated on the metallocene.

Assignment of the lowest energy transition at  $15900 \text{ cm}^{-1}$  (in CH<sub>2</sub>Cl<sub>2</sub>) in the visible spectrum of the ferricenium ion and ferrocenium derivatives to a LMCT  $({}^{2}E_{2} \rightarrow {}^{2}E_{1})$ , corresponding to a  $e_{1} \rightarrow e_{2}$  one-electron transition, is well-founded [1,21,22]. Clearly, the same one-electron assignment  $e_1$ -a  $\rightarrow e_2$ -a (Fig. 5) can be made for the lowest energy transition observed for these 17e dyads. What makes the LMCT energies so remarkable is the magnitude of their red-shift from the  ${}^{2}E_{2} \rightarrow {}^{2}E_{1}$  transition in Fc<sup>+</sup> (e.g.  $8200 \text{ cm}^{-1}$  for  $2f^+$ ). Previous work has found that the 'ferrocenium' transition is red-shifted by donor Cpsubstituents [17]. Substitution by two butyl groups causes a red-shift of 800 cm<sup>-1</sup> for example [20], and with the strong donor, N(*p*-tol)<sub>2</sub> the red-shift is  $3250 \text{ cm}^{-1}$  in CH<sub>3</sub>CN with negative solvatochromism  $\Delta E_{solv} = 427 \text{ cm}^{-1}$  for CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>CN [11]. Aryl groups are not strong donors so we need to look to the electronic configuration for an explanation of the large red shifts. From the DFT calculations both the singly occupied HOMO and, especially the HOMO -2, are the strongly perturbed orbitals because of conjugation of



Fig. 5. NIR band assignment for  $1d^+$ ; CH<sub>2</sub>Cl<sub>2</sub>, 15000–8000 cm<sup>-1</sup>.

a C $\equiv$ C-R group to the ferrocenvl ring. It is reasonable to assign the donor energy level as one related to the e1-a orbital and the energy of this will be heavily dependent on the ionization potential of the C=CR group. In the excited state the acceptor energy level, approximated by the  $[Fc]^{+/0}$  potential, while perturbed strongly by the incorporation of the  $C \equiv C$ , is relatively invariant with any group. Therefore, the linear correlation of the CT energies seen in Fig. 4 is consistent with an assignment of a HOMO -3 $(donor) \rightarrow HOMO$  (acceptor) CT transition. While a description as an LMCT transition is appropriate it is important to recognise that the contribution of the  $C \equiv CR$  $\pi$  orbital to the donor and acceptor levels depends on the ionization energy of this  $\pi$  orbital. For the small ring aryl, the donor level has a significant input from the C  $\equiv$  CR  $\pi$ orbital; the reverse holds for the acceptor level.



Fig. 4. Correlation of CT energies with oxidation potential of aryl group; CH<sub>2</sub>Cl<sub>2</sub>.

New bands in the OTTLE UV-Vis spectra above  $22000 \text{ cm}^{-1}$  were generally shoulders on the intense aryl transitions and were not studied in detail nor were the weak transitions which were observed (Fig. 3) from  $20000 \text{ cm}^{-1}$ to the LMCT band. The energy of some was dependent on the annelation of the ring and were solvatochromatic. Of greatest interest were the weak bands at  $\sim 17200 \text{ cm}^{-1}$ the energy of which varied little with aryl and were not solvatochromic (Table 2). These weak bands are assigned to HOMO-LUMO transitions (Fig. 5) but because both energy levels have considerable aryl character they cannot be described as spin-allowed d-d transitions as is the case for FcH<sup>+</sup> [1,21,22,24]. The calculated HOMO-LUMO gap for the 17e species is significantly smaller than for the corresponding 18e, consistent with the lower energy for the HOMO-LUMO transition in the 17e species.

#### 4. Conclusion

Perturbation of a ferrocenyl moiety by an unsaturated  $RC_2$  or  $RC_4$  (R = aryl) group leads to an increase in the energy of the ferrocenyl  $\pi$  bonding orbitals such that the frontier orbital configuration for both 17e and 18e species has the dyad  $\pi$  orbitals at HOMO and HOMO – 2. The relative importance of the aryl contribution to the  $\pi$  orbitals is dependent on the ionization potential of the -C=CR group and the HOMO has a significant aryl contribution with large annelated rings. Both the HOMO and HOMO -2 provide a delocalised system for communication between the ferrocenyl and aryl groups but the experimental data suggest that there is not a strong  $\pi$  interaction in the ground state. Low-energy LMCT are ubiquitous in 17e (metallocenyl)<sup>+</sup>- $C_n R$  systems; R is a formal  $\pi$  donor and includes aromatic derivatives such as naphthalimide [13] generally regarded as acceptors. A wide range of metallocenyl groups, e.g. n- $C_5H_4Ni(PPh_3)$  [25],  $\eta$ - $C_5H_4Co(Ph_4C_4)$  [26] can be involved. As the LMCT energies range from 12500 to 4000 cm<sup>-1</sup> these systems represent a tunable electrochromic series. The challenge is to increase the intensity of the LMCT bands.

## 5. Experimental

The synthesis and characterisation of the compounds discussed herein have been published elsewhere [16]. *Calculations:* All *ab initio* calculations were performed using the B3LYP hybrid density functional theory with a 6-31G(d) basis set. All calculations were run within Spartan '02 and then QChem quantum module. The unrestricted B3LYP was used for calculations on the non-18 electron systems. *Spectroelectrochemistry:* Cyclic and square wave voltammetry in CH<sub>2</sub>Cl<sub>2</sub> were performed for all compounds using a three-electrode cell with a polished disk, Pt (2.27 mm<sup>2</sup>) as the working electrode; solutions were ~10<sup>-3</sup> M in electroactive material and 0.10 M in supporting electrolyte (triply recrystallised TBAPF<sub>6</sub>). Data were recorded on an EG&G PAR 273A computer-controlled potentiostat. Scan rates of 0.05–1 V s<sup>-1</sup> were typically employed for cyclic voltam-

metry and for Osteryoung square-wave voltammetry, square-wave step heights of 1–5 mV, a square amplitude of 15–25 mV with a frequency of 30–240 Hz. All potentials are referenced to decamethylferrocene;  $E_{1/2}$  for sublimed ferrocene was 0.55 V. EPR spectra were obtained using a Bruker EMX X-band spectrometer equipped with a Bruker variable temperature accessory, a Systron-Donner microwave frequency counter and a Bruker gaussmeter; ca 5 mM THF/TBAPF<sub>6</sub> solutions of the compound were reduced electrochemically *in situ*.

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