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Electronic and optical properties of conjugated group 8 metallocene derivatives

Stephen Barlow[a] **and Seth R. Marder**[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR.*
E-mail: stephen.barlow@chem.ox.ac.uk
[b] *Department of Chemistry and Optical Science Center, University of Arizona, Tucson, AZ 85721, USA*

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Ferrocene and ruthenocene have been incorporated into a range of conjugated systems. The interaction of these metallocene donor moieties with conjugated substituents is more complex than that of organic donors; both metal-based and ligand-based orbitals of the metallocene interact with the orbitals of the π-system. Here we review the rôle of these interactions in giving rise to a variety of interesting properties including non-linear optical activity in donor–acceptor systems, mixed-valence behaviour in bis(ferrocenyl) compounds, and structural distortions in polymethines.

Introduction

While derivatives of ferrocene and, to a lesser extent, ruthenocene are one of the most widely studied classes of organometallic compounds (work on osmocene derivatives has been much more limited), a detailed understanding of the electronic structure of conjugated metallocene derivatives has only recently emerged. Here we survey some the electronic and optical properties of conjugated metallocene derivatives, illustrating how similarities in the electronic structure can be used to draw parallels between what may appear to be somewhat disparate sets of observations. We hope to highlight aspects of the structure–property relationships for metallocene derivatives which are unique and are not found in conjugated organic materials.

Steve Barlow was born and raised in Hampshire and Dorset. He obtained BA and DPhil degrees in Chemistry in 1992 and 1996 respectively, both from the University of Oxford. After postdoctoral work with Seth Marder at the California Institute of Technology, he returned to Oxford in 1998 as a temporary lecturer in the Inorganic Chemistry Laboratory and a tutorial fellow at Lady Margaret Hall. His research interests include optical, electronic and magentic properties of organometallic and unsaturated organic systems, and understanding how these properties are related to electronic structure.

Seth Marder was born and raised in New York city. He obtained his Bachelors of Science in Chemistry from Massachusetts Institute of Technology in 1981 and his Doctorate, in Chemistry, from the University of Wisconsin-Madison in 1985. After postdoctoral studies at Oxford and at the California Institute of Technology and the Jet Propulsion Laboratory, he become a Member of the Technical Staff at the Jet Propulsion Laboratory and a Member of the Beckman Institute at the California Institute of Technology. In 1998 he moved to the University of Arizona, where he is a Professor of Chemistry and Optical Science. His research interests include liquid crystals, transport phenomena, multiphoton processes in organic and organometallic materials, and labels for biological imaging.

Electronic structure of metallocenes and their conjugated derivatives

Firstly we will briefly review the electronic structure of metallocenes, and the perturbation to this structure induced by substitution with an electron-withdrawing conjugated system. The three highest filled levels of ferrocene are derived from the d_{xy}, $d_{x^2-y^2}$ (e_{2g} in staggered $\{D_{5d}\}$ geometry) and the d_{z^2} (a_{1g}) orbitals (the HOMO of the neutral molecule is a_{1g}, whilst the SOMO of the cation is e_{2g}). The e_{2g} orbitals are somewhat δ-back-bonding, through interaction with combinations of the cyclopentadienyl (Cp) anion LUMOs, whilst the a_{1g} has some interaction with the metal s orbital and with the Cp rings. Nonetheless, these orbitals may be regarded as essentially metal-based. The next highest orbitals (e_{1u}) of the metallocene are principally ligand-based, possibly with some contribution from the p_x and p_y metal orbitals. The lower energy orbitals involve bonding combinations of Cp orbitals with the metal d_{yz}, d_{xz}, s and p_z orbitals and do not concern us further. The LUMO of ferrocene has symmetry e_{1g} (in D_{5d}) and is derived from an out-of-phase π interaction between the d_{xz}/d_{yz}, and Cp orbitals.

The bonding in ruthenocene (and osmocene) is qualitatively the same, but UV-photoelectron spectra reveal substantial differences in metal-based orbital energies. The first vertical ionisation potentials (IPs) for ferrocene and ruthenocene are 6.86/6.89 and 7.45 eV, respectively,[1,2] whilst the highest ligand-based levels lie at rather similar energies with e_{1u} vertical ionisations at 8.72/8.77 and 8.47/8.51 eV, respectively. Thus, ferrocene is clearly the stronger donor in an electron-transfer sense. Methylation of the cyclopentadienyl rings raises the energy of both the filled d-orbitals (the first IP of decamethylferrocene is 5.88 eV) and the highest ligand-based orbitals (lowest ligand ionisation of decamethylferrocene is 7.31 eV). For comparison, the first IPs of *N*,*N*-dimethylaniline and anisole are 7.45 and 8.42 eV, respectively,[3] indicating that these compounds are weaker electron-transfer donors than ferrocene. However, it does not necessarily follow that a stronger electron-transfer donor will lead to a greater perturbation of an attached π-conjugated system, since the detail of the electronic coupling between the donor and the π-system is also critical (*vide infra*).

When a conjugated system is attached to a metallocene the most significant perturbation is *not* to the metal-based HOMOs. Consider a ferrocene derivative with a moderately electron-withdrawing conjugated substituent, such as **1** (Fig. 1). The first IP (6.97 eV) and electrochemical oxidation potential (+25 mV *vs*. ferrocenium/ferrocene in THF) of **1** are close to those of ferrocene.[4] Similar electrochemical results have been found in related systems.[5,6] The highest *ligand* level of the metallocene

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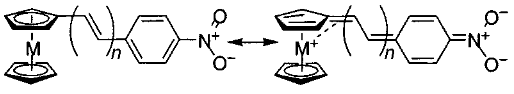


1, M = Fe, *n* = 1
2, M = Fe, *n* = 2
3, M = Ru, *n* = 1

Fig. 1 Neutral and charged resonance structures for nitrostyrene-substituted metallocenes.

(e_{1u}) shows a much greater perturbation; in **1** an ionisation is found at 8.36 eV, *i.e.* lower in energy than that e_{1u} ionisation of ferrocene, or the first ionisation of nitrostyrene. We attribute this ionisation to an orbital ('π') formed by an out-of-phase combination of one of the e_{1u} pair with the HOMO of the nitrostyrene fragment (as shown in Fig. 2).

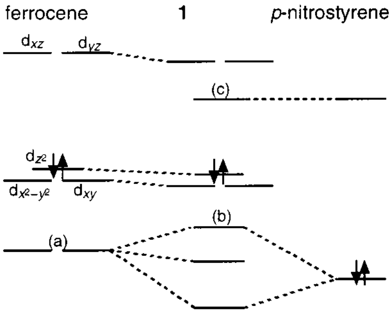


Fig. 2 Qualitative partial MO diagram showing interaction between the frontier orbitals of ferrocene and *p*-nitrostyrene fragments in **1**. The paired electrons indicate the HOMO for each compound. Orbital (a) is the highest filled Cp-based orbital of the metallocene (e_{1u} in D_{5d}), whilst (b) is the highest ligand-based orbital ('π') of **1** and (c) is the acceptor-based LUMO of **1**.

Compound **1** exhibits a molecular reduction at the same potential as *p*-nitrostyrene (−1670 mV *vs.* ferrocenium/ferrocene according to cyclic voltammetry in THF). The extended analogue **2** is reduced at −1635 mV, whilst nitrobenzene is reduced at −1730 mV. A similar chain length dependence of reduction potential was found for $[\mathrm{Mc(CH{=}CH)}_n\mathrm{C_7H_6}]^+$ (n = 0, 1, 2, 3; Mc = Fc {ferrocenyl}, Rc {ruthenocenyl}).[7] These results suggest that the LUMO is centred on the acceptor moiety, with some delocalisation onto the π-bridge (the empty d_{xz} and d_{yz} orbitals of the metallocene are at relatively high energy). An EPR study of $[\mathbf{1}]^{\bullet-}$ shows the unpaired electron to be largely localised on the nitrophenyl ring,[8] consistent with electrochemical data.

The orbital picture deduced from PES, electrochemical and EPR data above is consistent with that derived from extended-Hückel[9] and DF[4] calculations (see Fig. 3). This model can be successfully extended to other donor–acceptor metallocene derivatives (so long as the acceptor is sufficiently strong that the empty acceptor orbital lies below the metal d_{xz} and d_{yz} orbitals in energy). However, as the acceptor gets very strong it is necessary to further refine the simple model described above. Crystallographic and NMR data indicate that with electron-acceptors of moderate strength, the structure is well approximated by the neutral valence-bond picture (Fig. 1, left-hand structure). However, as the acceptor (or donor) is strengthened the zwitterionic resonance form gains in importance. This results in a reduction in the bond-length alternation (BLA) of the alkene bridge. Although there are apparently no crystallographically characterised examples of metallocene derivatives with a strong acceptor such as that in compounds **4**–**9**, the effect is manifested in NMR spectra. For example, in compound **4** (strong acceptor) the polyene protons show coupling constants of *ca.* 13 Hz over both formally double and formally single bonds, whilst in $\mathrm{Fc''(CH{=}CH)_2CHO}$ {Fc″ = 2,3,4,5,1′,2′,3′,3′-octamethylferrocen-1-yl, $\mathrm{(C_5Me_4H)Fe(C_5Me_4)}$} (weak acceptor) coupling constants alternate between *ca.* 15 Hz across formally double bonds and *ca.* 10 Hz across formally single bonds. More evidence for the increased importance of the charge-transferred resonance form in strong-acceptor compounds comes from electrochemistry: **5** is oxidised at +325 mV *vs.* ferrocenium/ferrocene in THF, suggesting a much more severe effect of the acceptor on the metal than in the nitrophenyl analogue, **1**. Moreover, the effect is strongly chain-length dependent; the potentials for **6** and **7** are +200 and +110 mV, respectively, indicating a decrease in donor–acceptor coupling as the chain length increases.[4]

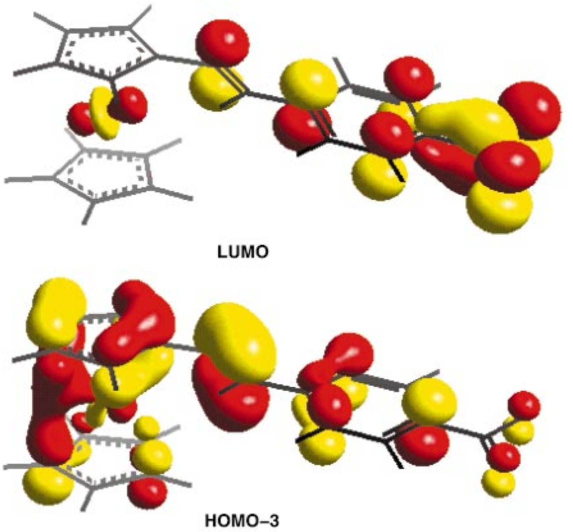
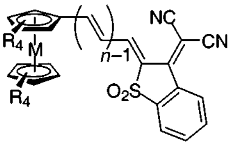
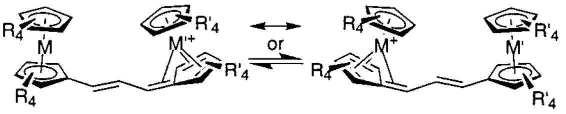


Fig. 3 The LUMO and the highest filled ligand-based π-level of **1** according to DF calculations; the three highest-filled levels are all principally metal d in character.[4]



4, M = Fe, R = Me, *n* = 3
5, M = Fe, R = H, *n* = 1
6, M = Fe, R = H, *n* = 2
7, M = Fe, R = H, *n* = 3
8, M = Fe, R = H, *n* = 4
9, M = Ru, R = H, *n* = 3

A broadly similar picture is revealed by DF calculations for the bis(metallocenyl)allylium cations ($[\mathbf{10}]^+$–$[\mathbf{14}]^+$); here the LUMO is the π* orbital of the unsaturated bridge (Fig. 9).[10] A similar picture of filled d-orbitals above an extended π-level presumably applies to bis(metallocenyl)polyenes, polyynes and arylenes, although, where the π-system is not particularly electron-poor, the LUMO may be the empty d_{xz}/d_{yz} orbitals rather than π*.



$[\mathbf{10}]^+$, M = M′ = Fe, R = R′ = H
$[\mathbf{11}]^+$, M = M′ = Fe, R = R′ = Me
$[\mathbf{12}]^+$, M = M′ = Ru, R = R′ = H
$[\mathbf{13}]^+$, M = M′ = Fe, R = H, R′ = Me
$[\mathbf{14}]^+$, M = Fe, M′ = Ru, R = R′ = H

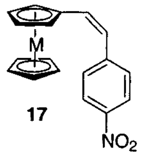
In many donor–acceptor systems there is little evidence to distinguish between the donor strengths of ferrocene and ruthenocene. For example, **7** and **9** are reduced at experimentally identical potential (−880 mV *vs.* ferrocenium/ferrocene in THF), indicating comparable contributions of the charge-transferred resonance form in each case (the octamethylferrocenyl group is clearly a stronger donor; the reduction potential of **4** is −960 mV).[4] However, comparison of the dipole moments of **1** (4.5×10^{-18} esu) and **3** (5.3×10^{-18} esu)[9] does suggest a slightly larger zwitterionic contribution in the ruthenium case. Systems with even stronger acceptors, such as 1,3-bis(metallocenyl)allylium cations, provide electrochemical evidence that, despite having a lower energy HOMO than ferrocene, ruthenocene is the stronger donor in conjugated systems. Thus, **[10]**$^+$ is reduced at −670 mV (*vs.* ferrocenium/ferrocene in THF), whilst **[12]**$^+$ is reduced at −715 mV (**[11]**$^+$ is reduced at −930 mV).[10] Crystal structures of [FcCHRc]$^+$[PF$_6$]$^-$ [11] and **[14]**$^+$[PF$_6$]$^-$ [10] show ruthenium coordination well approximated as η^6-fulvene : η^5-cyclopentadienyl, whilst the ferrocene centres are 'normal'. Thus, the superior donor properties of ruthenocene in this type of system can be attributed to the more extensive d-orbitals of ruthenium and its consequent tendency to shift towards η^6-fulvene coordination. It seems the difference in donor strength between ferrocene and ruthenocene are most evident when η^6-fulvene is an important resonance structure.

Linear and non-linear optical properties of conjugated metallocene–bridge–acceptor compounds

Much of the work on donor–acceptor conjugated metallocenes has been directed towards maximising and understanding their second-order NLO properties. Second-order NLO phenomena include frequency doubling and the linear electrooptic effect (*i.e.* electric-field-dependence of refractive index). For these properties to be observed, a non-centrosymmetric array of non-centrosymmetric molecules is required. The relevant molecular parameter is the first hyperpolarisability, β. The perturbation-theory-derived two-level model relates the static hyperpolarisability $\beta(0)$ to the characteristics of low-lying electronic excited states through eqn. (1):

$$\beta(0) \propto (\mu_{\mathrm{ee}} - \mu_{\mathrm{gg}})\frac{\mu_{\mathrm{ge}}^2}{E_{\mathrm{ge}}^2} \qquad (1)$$

where μ_{ee} and μ_{gg} are excited and ground-state dipole moments respectively, μ_{ge} is the transition dipole linking ground and excited states, and E_{ge} is the energy difference between the two states.[12] The two-level model does not apply to all classes of chromophore; for example, the non-linearity of octopolar molecules, where $\mu_{\mathrm{ee}} = \mu_{\mathrm{gg}} = 0$, depends on three-level terms.[13] Eqn. (1) indicates that intense low-energy charge-transfer transitions should lead to large β. The prototypical chromophore is the 'push–pull' donor–(conjugated bridge)–acceptor; good examples are (*E*)-4-(methoxy)-4′-nitrostilbene **15** and (*E*)-4-(dimethylamino)-4′-nitrostilbene **16**. In analogy, ferrocene was used to replace the organic donors of **15** and **16**; **17** was found to have a powder second-harmonic generation (SHG) efficiency 62× that of urea,[14] and even larger values of 123× and 200× urea have been reported for **18**[15] and **[19]**$^+$[I]$^-$ [16] respectively. Much other early work relied on powder SHG data. However, results are inherently subject to the vagaries of crystallisation; a large β chromophore will give zero SHG if it crystallises in a centrosymmetric space group. Resolved chiral chromophores have also been used;[17] these *must* crystallise in non-centrosymmetric space groups, but the molecules may still pack in such a manner that the hyperpolarisabilities of neighbouring molecules still largely cancel each other out, leading to low SHG responses. To understand relationships between molecular structure and molecular NLO properties, values of β are more useful. For non-ionic polar chromophores in solution, electric field-induced second-harmonic generation (EFISH)[18] can be used to measure $\mu\beta_\mu$, the scalar product of the permanent dipole moment (μ) and the vectorial part of the β tensor. Combined with a determination of μ, values of β_μ, the projection of the vectorial part of β onto the axis of μ, can be determined. $\mu\beta_\mu$ itself is also a figure-of-merit for the second-order NLO activity of a material where non-centrosymmetry is achieved *via* electric-field poling of a polymer matrix. Poling is carried out above the glass-transition temperature of the polymer, and the resulting polar order is 'frozen' in by cooling back below the glass transition. This means of achieving polar order is currently the most widely used approach for fabricating non-centrosymmetric materials for second-order NLO applications. More recently hyper-Raleigh scattering (HRS)[19] has also been used to measure β; the technique can be applied to ionic or octopolar chromophores, but great care must be taken to correctly account for the other non-linear optical effects which can contribute to the observed signal.



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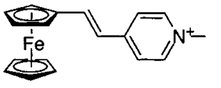
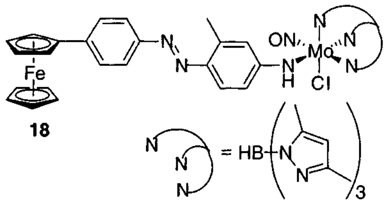


[19]$^+$



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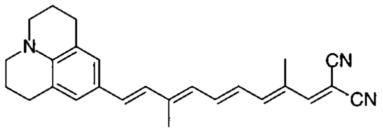
A wide variety of metallocene–donor–acceptor compounds have been synthesised; in addition to traditional organic acceptors, main group moieties,[20] transition-metal coordination complexes,[6,21–23] and organometallic groups[24–28] have been used as acceptors. The second-order NLO properties of a selection of these compounds are summarised in Table 1, along with absorption maxima.



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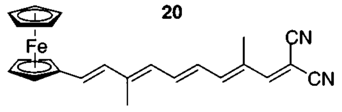

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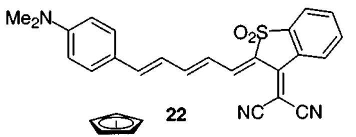

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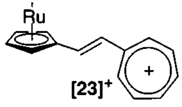
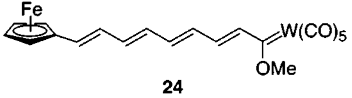


[23]$^+$



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Comparison of β or $\mu\beta$ values between chromophores is complicated by the fact that eqn. (1) relates to the static (dispersion-free) hyperpolarisability. The hyperpolarisability is greater (dispersion-enhanced) if the fundamental radiation employed in the measurement, or the frequency-doubled radiation generated, is close in energy to the energy of the excited state(s) responsible for the NLO behaviour. In the case of metallocene compounds, the contributions of more than one excited state to the non-linearity means that correction for dispersion cannot be made according to the two-level model (nevertheless, estimates have been made for some compounds and are included in Table 1).

To understand the origin of the NLO properties of a class of compounds it is necessary to understand the characteristics of the excited state or states contributing to the hyperpolarisability *via* eqn. (1). The quantities in eqn. (1) can be probed by optical

Table 1 Comparison of second-order NLO properties of some metallocene and organic molecules

Compound	λ_{max}/nm	$\mu\beta/10^{-48}$ esu	$\mu\beta(0)/10^{-48}$ esu	$\beta^{a}/10^{-30}$ esu	$\beta(0)^{a}/10^{-30}$ esu	Method	Ref.
15	370	153		34		EFISH, 1.907 μm ($CHCl_3$)	29
16	430	482	363	73	55	EFISH, 1.907 μm ($CHCl_3$)	30
1	356, 496	140		31		EFISH, 1.907 μm (*p*-dioxane)	9
3	350, 390	64		12		EFISH, 1.907 μm (*p*-dioxane)	9
20	570	5 500	3220			EFISH, 1.907 μm (acetone)	31
21	458[b]	4 600	3300			EFISH, 1.907 μm (acetone)	31
5	419, 667	160		29		EFISH, 1.907 μm ($CHCl_3$)	32
7	517, 746	3 000		405		EFISH, 1.907 μm ($CHCl_3$)	32
8	552, 743	11 200				EFISH, 1.907 μm ($CHCl_3$	32
22	744	10 500	3900			EFISH, 1.907 μm (CH_2Cl_2)	33
[**23**]$^+$[PF_6]$^-$	477, 642			362[c]	105	HRS, 1.064 μm (CH_2Cl_2)	7
24	541[b]			780[d]		HRS, 1.064 μm (hexane)	28

[a] EFISH values are β_μ; HRS values are $\langle\beta\rangle$. [b] For long-chain lengths, the highest π-level may approach the metal-based HOMO in energy and the two transitions may overlap; clearly this will happen at shorter chain length for ruthenocene compounds. [c] 640 × 10^{-30} esu in $MeNO_2$. [d] 2420 × 10^{-30} esu in acetonitrile.

spectroscopy. The most striking characteristic of the metallocene compounds, in contrast to their all organic analogues, is the presence of *two* relatively low-energy bands (Fig. 4). In most of the metallocene compounds both bands show positive solvatochromism (red shifts with increasing solvent polarity), suggesting that the corresponding transitions are both associated with increases in dipole moment.[34]

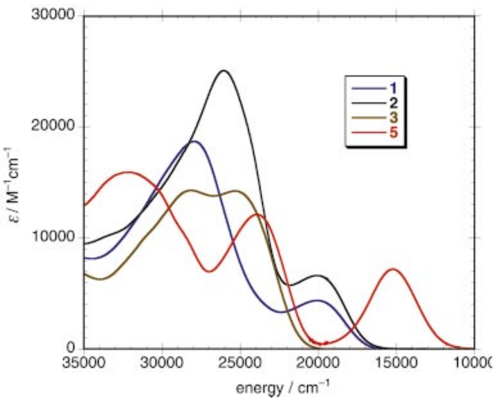


Fig. 4 UV–VIS–NIR spectra of several metallocenyl second-order NLO chromophores showing the effects on the spectra of chain length (**1** *vs*. **2**), replacing Fe with Ru (**1** *vs*. **3**), and acceptor strength (**1** *vs*. **5**).

Recently, Stark spectroscopy has been used to confirm that both transitions are indeed associated with dipole moment changes; in both **2** and **4** the lower energy (LE) band was found to have the larger $|\Delta\mu|$. Combining the observed ratio of $|\Delta\mu|$ with the transition energies and oscillator strengths, the relative contributions of the two excited states to the second-order NLO response can be estimated according to eqn. (1). In **2** the higher energy (HE) transition dominates β (63% of the two-level contributions). In the strong-acceptor compound **4** the relative importance of the two transitions is reversed (75% from LE transition).[4]

If one wishes to predict the effect of changes in molecular structure upon the optical spectrum, and hence upon the NLO behaviour, it is important to assign the two bands. We have recently suggested an assignment based on the orbital scheme described for **1** in the previous section, *i.e.* that the LE transition is metal-to-acceptor (HOMO-to-LUMO), whilst the HE transition is π-to-acceptor.[4] In contrast to previous assignments,[9,35] this model is consistent with *both* the larger $|\Delta\mu|$ of the LE transition, and with the changes in the spectra seen as the structure of the molecule is modified. The relatively high absorptivities observed for the LE band, despite poor metal–acceptor interaction, can be rationalised in terms of intensity stealing from the HE band. This intensity stealing should be most pronounced when the energy differences between the two excited states and between the ground and second excited state are minimised. This is seen experimentally; for example, the oscillator strengths of the LE and HE transitions of **1** are *ca*. 0.60 and 0.10 respectively, whilst for **5** (where the stronger acceptor leads to a smaller second excited state/ground state separation) the relevant values are 0.40 and 0.18.[36]

Many studies show the same factors used in organic chromophore design are operative in metallocene chrmophores; Table 1 gives some examples of the effects of acceptor strength and chain length, as well as of changing ferrocene for ruthenocene. It should be noted, however, that in analogy with organic compounds,[37] if the donor and/or acceptor strength is increased sufficiently, a point of optimised β will be obtained, corresponding to an optimised BLA, *i.e.* optimised mixture of neutral and charge-transferred resonance forms. The data in Table 1 show that metallocene chromophores can exhibit large β and $\mu\beta$ values of similar magnitude to the best all-organic chromophores. However, metallocene derivatives with high β or $\mu\beta$ absorb at very low energies; both the energies and broadness of the absorptions are factors which would limit the utility of metallocene chrmophores in devices designed for use at the telecommunications wavelengths of 1.3 and 1.55 μm. Nonetheless, films obtained by poling **1** and **2** in polymethylmethacrylate at 120 °C, showed electro-optic coefficients in excellent agreement with the values predicted from the EFISH-derived $\mu\beta$ values using an oriented gas model. The results indicate that the more three-dimensional shapes and lower oxidation potentials of ferrocene chromophores relative to traditional all-organic chromophores do not lead to any special complications.[38] Metallocene chromophores have also been covalently incorporated into a variety of polymers; the long-term orientational stability of these polymers after poling has been monitered by SHG measurements.[38–40]

We have seen that metallocene chromophores can exhibit large β and $\mu\beta$ values, but do metallocene chromophores offer any significant advantages over organic compounds for NLO applications? Comparing **1** and **15**, which have similar $\mu\beta$ and β, we find the ferrocene compound shows distinct disadvantages owing to the decreased transparency arising from its lower energy absorption band, as mentioned above. The ruthenocene analogue **3** shows superior transparency, but lower β. For the same bridge/acceptor motif, it seems that the ferrocenyl donor gives poorer β and $\mu\beta$ than *p*-dimethylaminophenyl (**1** *vs*. **16**; **7** *vs*. **22**). The LE excited state of **1** is lower in energy than the excited state of **16** (since ferrocene is a stronger electron-transfer donor), but the corresponding transition is much less intense (due to poor metal–acceptor interaction); as in **2**, the HE state is presumably the major contributor to β in **1**. In the stronger acceptor compound **7** the LE ferrocene band is much more important for β; however, it is no longer significantly lower in energy than that of its organic analogue **22**. Both **7** and

22 will show more contribution from the zwitterionic resonance form than **1** and **16**; we suggest this effect is more important for **22** (dimethylaminophenyl is a more effective donor for perturbing the electron density of a π-system than ferrocenyl), leading to larger μ and low energy absorption in the all-organic case. It is, however, possible that with even stronger acceptors, where dimethylaminophenyl compounds will have passed the point of optimal BLA, the ferrocene compound may actually give larger β.

We know of no reports of a bulk material based on a metallocene chromophore with non-linear optical properties rivalling those of the best all-organic materials. In addition, organometallic chromophores have not yet been shown to exhibit thermal[41,42] and photochemical[43] stabilities comparable to the some of the better all-organic systems; these factors are crucial to the fabrication of long-term performance devices. Thus, there is still a clear challenege to the organometallic chemist to demonstrate a specific advantage for using metallocene chromophores in second-order NLO applications.

In addition to the NLO-related studies described above, several other studies have focussed on other aspects of the spectroscopy of metallocene–(π-bridge)–acceptor compounds. Toma *et al.*[44] found the low-energy bands of (*E*)-FcCH=CHAr (Ar = aryl) were similar to those of ferrocene, with some dependence upon the Hammett coefficients of the substituent, except where Ar bore a strongly mesomerically electron-withdrawing substituent (*p*-CHO, *p*-CN, *p*-NO_2). These observations are consistent with our assignment of the spectra of **1**; presumably, in the former class of compounds the d–d transition is lowest in energy, whereas in the latter class the LUMO is acceptor-based. The complexes $[(\text{ferrocenylpyridine})Ru(NH_3)]^{3+}$ could also be regarded as metallocene–donor–acceptor complexes, the LUMO here being the part-filled t_{2g}-like orbitals of Ru^{III}. The low-energy band has accordingly been assigned to a $Fe^{II} \rightarrow Ru^{III}$ transfer, and analysed to show much stronger metal–metal coupling in the $[(4\text{-}FcC_5H_4N)Ru(NH_3)]^{3+}$ than in $[(3\text{-}FcC_5H_4N)Ru(NH_3)]^{3+}$.[45] Derivatives of [**19**]$^+$ have been used as indicators in rapid screening of hydrogenation catalysis.[46]

Electronic and optical properties of bis(metallocenyl)polyenes and related compounds

In this section we consider systems where two (or more) metallocene units are linked by alkene, alkyne or arene bridges. Ferrocene systems have been attractive candidates for studying mixed-valence behaviour,[48] since ferrocene has a well-developed organic chemistry, allowing attachment to a wide variety of bridges, and since both ferrocene and the ferrocenium ion are relatively stable. When linked conjugated ferrocenes undergo one-electron oxidation, a hole is introduced into the e_{2g} d-orbitals of one of the ferrocene moieties. The lowest energy band in the UV–VIS–NIR spectra is thus a transition from the highest filled d-orbital of the Fe^{II} moiety to the partially occupied orbital of the Fe^{III} moiety. In cases where the electronic coupling, V, between the Fe^{II}/Fe^{III} wavefunction (Φ_A) and the Fe^{III}/Fe^{II} wavefunction (Φ_B) is small compared to the reorganisation energy, λ, the strength of this intervalence charge-transfer (IVCT) band can be analysed to afford V and the interaction parameter, α.[48] according to eqn. (2) where Ψ is the

$$\Psi = (1 - \alpha^2)^{0.5}\Phi_A + \alpha\Phi_B \qquad (2)$$

ground state wavefunction. In bis(ferrocenyl) conjugated systems it generally seems that the assumption of small coupling is valid. The values of α and V in Table 2 allow one to compare the efficacies of various bridges at mediating electronic coupling. Electrochemical data are also included in Table 2; interpretation of $\Delta E_{1/2}$ data is less straightforward than that of IVCT data ($\Delta E_{1/2}$ depends on stabilising factors in the Fe^{II}/Fe^{II}, Fe^{II}/Fe^{III} and Fe^{III}/Fe^{III} species, and on through-space electrostatic effects), but the value can provide a useful rough indication of the strength of metal–metal interaction.

Both optical and electrochemical data show more interaction for alkenes than alkynes. This result is consistent with linear and non-linear optical results on analogous ferrocene–bridge–acceptors with alkene and alkyne bridges [the LE absorption of (*E*)-FcCH=CHB$(mes)_2$ {mes = 2,4,6-trimethylphenyl} is lower in energy and more intense than that of FcC≡CB$(mes)_2$ and β_μ is larger[20]] and with calculations for all-organic mixed-valence compounds.[49] Arenes are rather poor at mediating metal–metal interactions; this is consistent with the disruption of donor–acceptor coupling effected by the introduction of aromatic moieties into organic second-order NLO chromophores.[50]

Bis(ruthenocenyl) compounds have been much less studied, presumably partly due to the irreversible redox chemistry of ruthenocene itself. Recently, however, it has been found that RcCH=CHRc, and a number of substituted derivatives, undergo chemically (though not electrochemically) reversible two-electron oxidations to diamagnetic bis(η^5-cyclopentadienyl-

Table 2 Data pertaining to metal–metal interactions in some bis(ferrocenyl) systems

Compound	$\Delta E_{1/2}{}^a$/mV	λ_{max} $(\varepsilon_{max})^b$/nm (M^{-1} cm^{-1})	α^c	V^d/meV
$Fc(CMe_2)_2Fc$	80[51]	None observed	—	—
(*E*)-FcCH=CHFc	140[52]	1750 (1200)[54]	0.09	63
	170[53]	2040 (1340)[53]	0.10	61
$Fc(CH{=}CH)_2Fc^e$	129[53]	1820 (1570)[53]	0.08	53
$Fc(CH{=}CH)_6Fc^e$	0[53]	1800 (1600)[53]	0.03	24
FcN=NFc	235[55]	1760 (375)[54]	0.05	35
FcC≡CFc	130[56]	1560 (670)[56]	0.07	56
$Fc(C{\equiv}C)_2Fc$	100[56]	1180 (570)[54]	0.04	42
$Fc_2C{=}CH_2$	—	1800 (200)[55]	0.004	2.8
$Fc_2C{=}O$	—	1280 (62)[54]	0.002	1.9
o-$Fc_2C_6H_4$	131[e,57]	1530 (91)[e,57]	0.03	25
m-$Fc_2C_6H_4$	90[e,57]	1210 (46)[e,57]	0.013	13
p-$Fc_2C_6H_4$	104[f,57]	1340 (620)[f,57]	0.046	43
[**10**]$^+$	180[58]	—	—	—
	610[10]			
$[Fc(CH)_5Fc]^+$	140[58]	—	—	—
	610[54]			
$[Fc(CH)_{13}]^+$	40[58]	—	—	—
[**11**]$^+$	700[10]	—	—	—

[a] Separation between successive ferrocene oxidations in CH_2Cl_2. [b] Absorption maxima and maxmium absorbtivity for the IVCT band of the mono-oxidised species in CH_2Cl_2. [c] Interaction parameter and [d] electronic coupling energy derived from analysis of the IVCT band according to $V = (2.05 \times 10^{-2}/r)(\varepsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2})^{1/2}$, where r is the intermetallic distance and $\Delta\bar{\nu}_{1/2}$ is the IVCT band width at half height, and $\alpha = V/\bar{\nu}_{max}$.[48] [e] In MeCN. [f] In $CHCl_3$.

ruthenium)(μ-η^6 : η^6-pentafulvadiene) dications (Fig. 5).[60,61] These formally ligand-based oxidations can be contrasted to the metal-based oxidations of iron analogues; presumably the small differences in energy between the highest π-orbital and the ruthenium d-orbitals is important (although di-Ru^{III} intermediates are postulated[61]), along with the greater tendency of ruthenium to adopt η^6 coordination and to retain an 18 electron configuration. Similar two-electron oxidations involving structural rearrangemnt of a ruthenocene to η^6-fulvene geometry, have been observed in RcC≡CRuCp(PPh$_3$)$_2$ and related compounds.[62,63] Even biruthenocene can be oxidised to the diamagnetic bis(η^5-cyclopentadienylruthenium)(μ-η^6 : η^6-fulvalene) dication under certain conditions.[64] In this respect, ruthenocene resembles an organic fragment more than does ferrocene. For example, the dication of *N*,*N*,*N′*,*N′*-tetramethylbenzidine has a quinoidal, and presumably diamagnetic, structure,[65] due to good mediation of N–N interaction by the π-system. By contrast, the dications of dinuclear bis(ferrocenyl) complexes typically behave as two more-or-less non-interacting spin 1/2 centres; the biferrocene dication has no significant exchange interactions between the two Fe^{III} centres.[66,67]

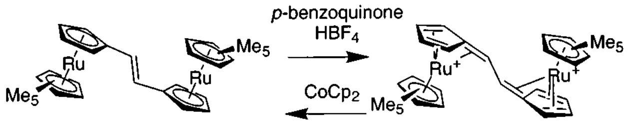


Fig. 5 Chemically reversible two-electron oxidation of a bis(ruthenocenyl) ethene.[58]

The metal–metal interactions possible in conjugated linked metallocenes have been exploited in poly(ferrocenylenevinylene)[68] and poly(ferrocenylenedivinylene)s;[69] when partially oxidised poly(ferrocenylenedivinylene) shows superior conductivity to similar polymers with more ‘insulating’ bridges.[69]

Electronic and optical properties of bis(metallocenyl)polymethines

In this class of compounds, two metallocenes are linked with an odd number of CH groups and there is an overall positive charge stabilised by contributions from (η^6-fulvene)(η^5-cyclopentadienyl)metal cation resonance structures. We have been studying symmetrical and unsymmetrical termethine {$n = 3$} examples with Fc, Rc and Fc″ end groups.[10,70,71] We have determined crystal structures for a number of these compounds. Whilst [**10**]$^+$[PF$_6$]$^-$ and [**11**]$^+$[PF$_6$]$^-$ showed symmetrical cations (as do a close trimetallic analogue,[72] and [FcCHFc]$^+$[BF$_4$]$^{-73}$), the crystal structure of [**12**]$^+$[PF$_6$]$^-$ showed a cation best described as a (η^6-fulvene)(η^5-cyclopentadienyl)ruthenium cation bridged by a vinylene moiety to a ‘normal’ ruthenocene, with BLA between formally single and double bonds of some 0.100(6) Å (Fig. 6). Moreover, the similarity of the IR and Raman spectra of [**12**]$^+$[PF$_6$]$^-$ in the solid state and in solution suggests the origin of this distortion is an intramolecular effect.

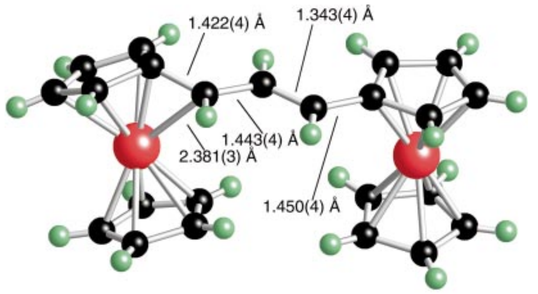
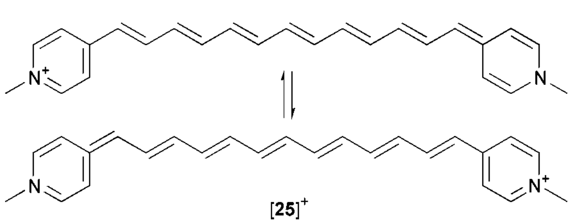


Fig. 6 The [**12**]$^+$ cation in the crystal stucture of its hexafluorophosphate salt.[10,70]

The only previous report of such a distortion is that reported by Tolbert and Zhao, who showed [**25**]$^+$ to be unsymmetrical in solution by comparing IR and UV–VIS spectra with those of lower homologues.[74,75] Such distortions afford bistable systems, which could form the basis for a switchable device, where a change in external electric field leads to a dramatic change in polarisation.



[**25**]$^+$

Unsymmetrical intramolecular localisation effects have been predicted to occur in long-chain (*ca*. 13 methine groups where the end group can stabilise the positive charge) all-organic polymethines,[74,76] and can be understood in analogy to the Peierls distortion,[76] or by analogy with mixed-valence chemistry.[49,74] We attribute the observation of localisation at low chain length for [**12**]$^+$ to the high reorganisation energy associated with the ruthenocene/(η^6-fulvene)(η^5-cyclopentadienyl)ruthenium system.

The electronic spectra of bis(metallocenyl)polymethines are strongly reminiscent of those of the metallocene donor–acceptor NLO dyes discussed earlier; *i.e.* there are two prominent transitions. Tolbert has synthesised the series [Fc(CH)$_n$Fc]$^+$[BF$_4$]$^-$ {$n = 1, 3, 5, 9, 13$}, and found the energy of the LE band to be inversely proportional to the conjugation length ($N_{\text{eff}} = n + 6$).[58] Fig. 7 shows this dependence, along with the stronger chain-length dependence of the HE band, which closely resembles that of the absorption of [Ph(CH)$_n$Ph]$^+$ cations. Thus, we assign the HE band as a π → π* transition. This is, of course, consistent with the assignment of the HE of metallocene–bridge–acceptor compounds as π → (acceptor), and with the orbital scheme. Assignment of the LE band as M → π* is consistent with the weaker chain-length dependence of this band, with the greater blue shift compared to that in the HE band seen on replacing iron with ruthenium (Fig. 8), with the analogous metallocene–bridge–acceptor compounds, and with the calculated orbital structure (Fig. 9). As shown in the calculated orbitals for the distorted [**12**]$^+$ cation, the highest π-level of unsymmetrical species is mainly from the cyclopentadienyl orbitals of the‘normal’ metallocene, whilst the π* LUMO is correspondingly displaced towards to the (η^6-

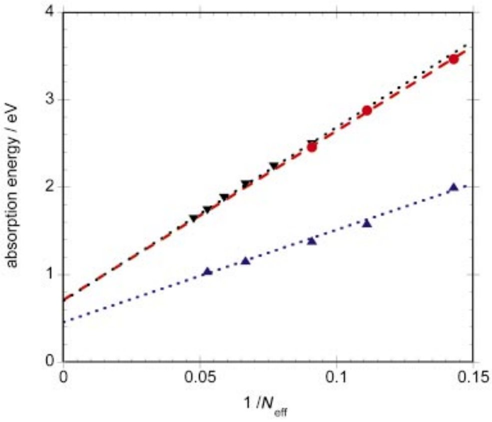


Fig. 7 Conjugation-length dependence of the absorption maxima of α,ω-bis(phenyl)polymethine cations (black; data from ref. 58), the LE (blue; data from ref. 58) and HE (red; data from refs. 10, 59 and 77) bands of α,ω-bis(ferrocenyl)polymethine cations. N_{eff} is defined as $n + 8$ for the phenyl compounds, and $n + 6$ for the ferrocenyl species.

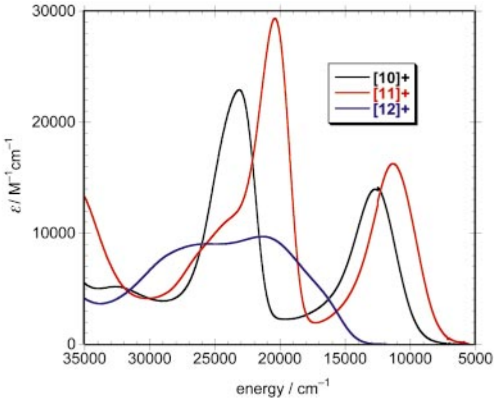


Fig. 8 UV–VIS–NIR spectra of three bis(metallocenyl)termethines, showing the effect of metallocene methylation ([**10**]$^+$ *vs.* [**11**]$^+$), and changing Fe for Ru ([**10**]$^+$ *vs.* [**12**]$^+$).

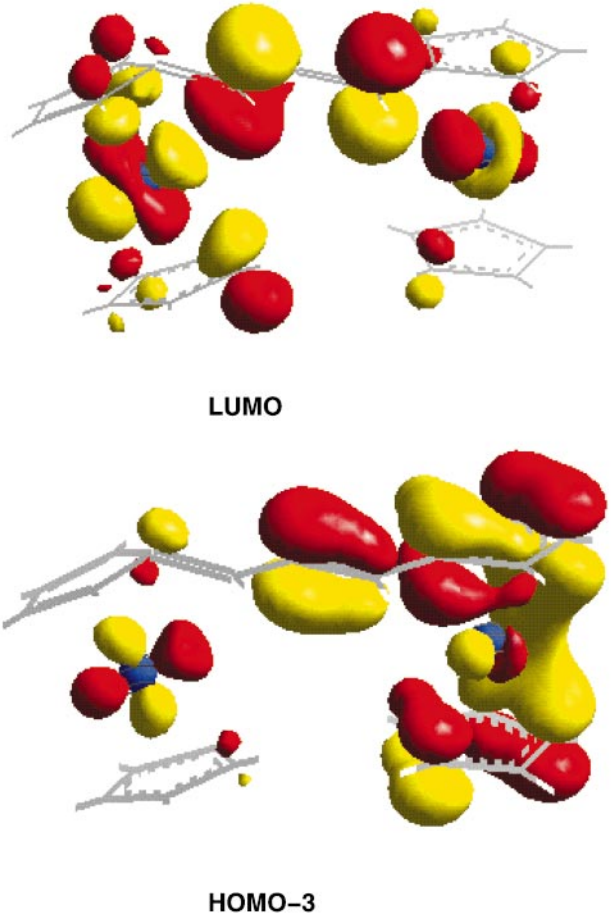


Fig. 9 The LUMO and the highest filled ligand-based π-levels of [**12**]$^+$ according to DF calculations; the three highest-filled levels are all principally metal d in character.[10]

fulvene)(η^5-cyclopentadienyl)metal end of the molecule. The HOMO is located on the 'normal' metallocene. Nevertheless, the orbitals of symmetrical and unsymmetrical bis(metallocenyl)termethines are broadly similar. The bis(metallocenyl)termethine series holds completely symmetrical species ([**10**]$^+$, [**11**]$^+$), somewhat unsymmetrical species ([**13**]$^+$, in which the octamethylferrocenyl group undergoes more distortion than the ferrocene, but the BLA is small), and fully bond-alternated structures ([**12**]$^+$, [**14**]$^+$). This variation is analogous to that found in donor–acceptor compounds, where one can tune between bond-equalised and fully bond-alternated structures through donor and acceptor strength.[37]

Summary

The work of numerous groups has demonstrated that conjugated group 8 metallocenes have a variety of interesting optical and electronic properties. Over the past several years it has become more clear that the metallocenes are different in their behaviour as π-electron donors from simple organic groups, such as those derived from anisole or aniline. In particular, a metallocene interacts with a conjugated π-system both through the cyclopentadienyl group and through the metal-based orbital. These various interactions create opportunities to control the coupling of the metal orbital with the π-system and to control the interaction between metal centres. While interesting non-linear optical and electronic properties have been reported, conjugated metallocenes have yet to find use in device applications. Perhaps, as our understanding of the electronic of this class of molecules become more complete, novel applications of these materials will be identified.

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