Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Triad and cyclic diad compounds of [60]fullerene with metallocenes†

Cite this: *Dalton Trans.*, 2013, **42**, 5056

Dorothée Mancel, Martyn Jevric, E. Stephen Davies, Martin Schröder* and Andrei N. Khlobystov*

Received 2nd November 2012,
Accepted 7th January 2013

DOI: 10.1039/c3dt32626h

www.rsc.org/dalton

Metallocene-bridged [60]fullerene triads and cyclised metallocene-[60]fullerene diads are formed *via* [3 + 2] cycloaddition reactions of [60]fullerene with metallocene dialdehyde and an amino acid. In the case of cyclic diads only one regioisomer is formed, as determined by UV-vis and NMR spectroscopic studies. These compounds have both electron donor (metallocene) and acceptor ([60]fullerene) components and give three electrochemically reversible one-electron reductions for each [60]fullerene moiety. For the ferrocene-containing compounds, an electrochemically reversible one-electron oxidation process is observed, with an irreversible oxidation observed for the ruthenocene analogues.

Introduction

Photoinitiated multistep electron transfer between donor and acceptor sites is essential to photosynthesis.[1] Conversion of solar energy into chemical energy involves three sequential photochemical events: (i) light absorption, (ii) excitation energy transduction and (iii) electron transfer.[2] The understanding of each of these key processes is of paramount importance for the development of efficient synthetic light-harvesting systems, with the ultimate goal of processing light energy to chemical or electrical equivalents for storage and use. Moreover, such knowledge is important in the development of molecular electronic devices for data storage, molecular switches, sensors, photoconductors and photoactive diads.[2]

One approach towards systems capable of artificial photosynthesis or that demonstrate novel molecular electronics is to design diads bearing covalently linked electron donor moieties in close proximity to the surface of electron acceptor [60]fullerene. The excellent electron accepting capacity of [60]fullerene, combined with a low reorganisation energy, makes it an attractive candidate as an active component for the conversion of light energy.

Unfunctionalised [60]fullerene is capable of accepting up to 6 electrons in six one-electron reduction steps, and this property is retained when the fullerene is functionalised with pyrrolidine groups *via* [3 + 2] cycloaddition.[3] [60]Fullerene promotes forward electron transfer from photoexcited electron donors while simultaneously retarding back electron transfer. Fullerenes also improve light-induced charge separation.[4,5] In particular, the delocalisation of charges (electrons or holes) within the rigid, icosahedral carbon cage of [60]fullerene (van der Waals diameter = 10 Å) is important in stabilising charged states,[6] and as a result, donor–acceptor molecular diads containing [60]fullerene are known to generate long-lived charge-separated states.[4,5] [60]fullerene is a moderate absorber in the visible region (ε = 10^2–10^3 dm^3 mol^{-1} cm^{-1} in the range λ = 400–900 nm),[7] and its functionalisation with external chromophores enhances the absorption of visible light in donor–acceptor diads and improves light-harvesting efficiency.[8–28]

In the search for molecules that can achieve efficient photoinduced charge separation and slow rates of charge recombination, numerous examples of molecular systems in which electron donors are covalently linked to [60]fullerene have been synthesised.[6,8] In addition to organic electron donors such as porphyrins,[9–15] phthalocyanines,[16,17] tetrathiafulvalenes[18–21] and carotenes[22] that have been attached to [60]fullerene, metallocenes such as ferrocene (Fc) and ruthenocene (Rc) have also been investigated.[23–28] These diads are charge neutral and soluble in common solvents allowing their electrochemical and photochemical properties to be studied in detail.

Due to the irreversible oxidative chemistry of ruthenocene,[29,30] ruthenocene-based donor–acceptor systems have received less attention than ferrocene analogues, and based on ionisation potentials, ferrocene (6.86 eV) is a stronger donor than ruthenocene (7.45 eV).[31,32] However, in some diads, this trend is reversed and ruthenocene acts as the stronger electrochemical donor.[33] This has been attributed to the involvement of the more extensive ruthenium 5d-orbitals[34] leading to an

School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK. E-mail: M.Schroder@nottingham.ac.uk, Andrei.Khlobystov@nottingham.ac.uk; Fax: +44 (0)115 9513563; Tel: +44 (0)115 9513490

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3dt32626h

increase in direct or indirect spatial overlap with the acceptor moiety.[35] Langa *et al.* have reported examples of ruthenocene-pyrrolidino[60]fullerene diads[36,37] and characterised their electrochemical properties. In this study, we have expanded this class of compound to include acceptor–donor–acceptor triads where the metallocene bridges two fullerene cages and investigated the spectroscopic and electrochemical properties of these novel fullerene derivatives.

Synthesis

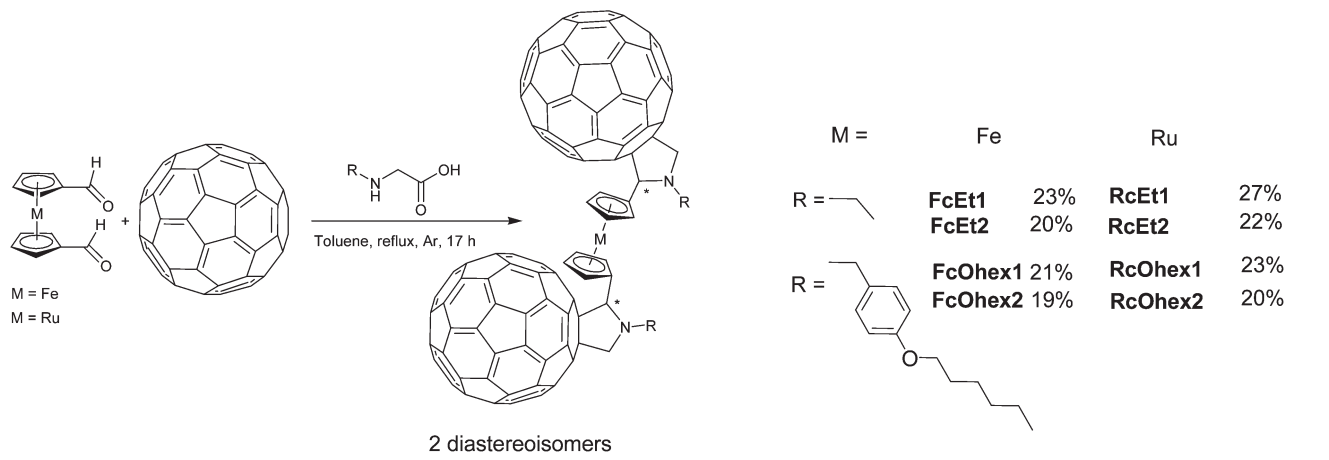
1,1′-Disubstituted metallocenes were selected as units to bridge pyrrolidine functionalised fullerenes formed by the Prato reaction.[38] The low solubility of compounds containing more than one fullerene cage has been highlighted as a key problem in the study of these materials. However, we have shown that *N*-(benzyl(hexyloxy))glycine, bearing a sterically bulky alkyl group, both accelerates the cycloaddition reaction with fullerenes and increases the solubility of the functionalised fullerene product.[39] Therefore, we utilised this amino acid for the preparation of fullerene–metallocene adducts in this study.

Typical reaction conditions employed for the double dipolar [3 + 2] cycloaddition require a ratio of fullerene : amino acid : dialdehyde of 3 : 4 : 1 in toluene. As reported for other Prato reactions, the use of excess amino acid increases the conversion rate of the reaction.[40,41] The progress of the reaction was followed by a colour change of the solution from magenta to brown, and thin layer chromatography (TLC) confirmed the formation of two products with similar R_f values corresponding to the formation of two diastereoisomers; each cycloaddition reaction forms a new stereogenic centre within the pyrrolidine groups (Scheme 1). The diastereoisomers were separated using gradient elution column chromatography (100% carbon disulfide → 100% toluene). Although the diastereoisomers were isolated in pure forms, it was not possible to assign the absolute stereochemical configuration of these products. The compound numbers in Scheme 1 refer to the order in which each diastereoisomer elutes from the chromatography column, *e.g.* **FcEt1**, **FcEt2**. The ^{1}H NMR spectrum of each diastereomer reveals one type of fulleropyrrolidine and cyclopentadienyl moiety, which indicates that the two parts of the molecule are related by a symmetry element on the metal atom.

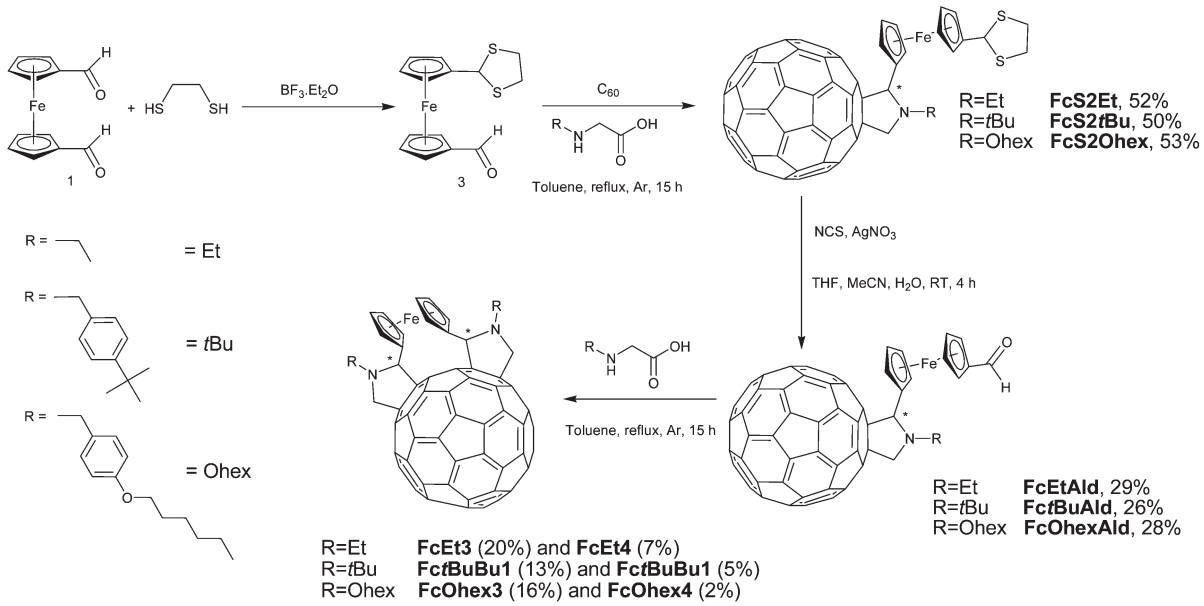
As expected, the triads **FcEt1**, **FcEt2**, **RcEt1** and **RcEt2** obtained from reactions with *N*-(ethyl)glycine show poor solubility, thus inhibiting their full characterisation. MALDI-TOF mass spectrometry shows molecular ions for each of these compounds with the observed isotopic distribution patterns matching the calculated patterns. The ^{1}H NMR spectra of **FcEt1**, **FcEt2**, **RcEt1** and **RcEt2** exhibit the characteristic pattern for protons of the pyrrolidine ring consisting of two doublets, at *ca.* δ 4.1 and 5.0 ppm ($^2J \sim 9.4$ Hz) for the CH_2 group, and a singlet at *ca.* δ 5.0 ppm assigned to the chiral CH centre. Hydrogen atoms of the cyclopentadienyl rings are non-equivalent and are observed as a group of signals between δ 4.0 and 5.5 ppm. ^{13}C NMR and other spectroscopic characterisations for **FcEt1**, **FcEt2**, **RcEt1** and **RcEt2** were hindered due to their limited solubility.

In contrast, the triads **FcOhex1**, **FcOhex2**, **RcOhex1** and **RcOhex2** synthesised from *N*-(benzyl(hexyloxy))glycine are highly soluble in $CHCl_3$, toluene and *o*-DCB (1,2-dichlorobenzene). The ^{1}H NMR spectra of these compounds show resonances characteristic of the pyrrolidine and metallocene groups (*vide ultra*). In addition, the benzyl CH_2 group appears as a pair of signals between δ 5.0 and 6.5 ppm ($^2J \sim 13.2$ Hz), arising from the proximity of the chiral centre of pyrrolidine, which results in magnetic inequivalence in the hydrogen atoms of CH_2 group.

^{13}C NMR spectroscopy of **FcOhex1** and **FcOhex2** and **RcOhex1** and **RcOhex2** did not distinguish between the respective pairs of diastereoisomers. Characteristic signals of the functionalised fullerene cage are observed between δ 130 and 160 ppm, and the two sp^3 carbon atoms of the fullerene cage within the pyrrolidine group appear at δ 68 and 78 ppm



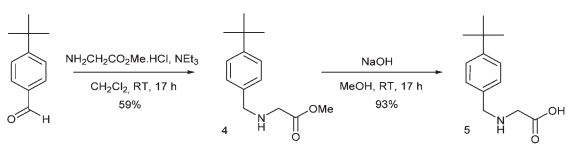
Scheme 1 Synthesis of diastereomeric pairs **FcEt1** and **FcEt2**, **FcOhex1** and **FcOhex2**, **RcEt1** and **RcEt2**, **RcOhex1** and **RcOhex2**.



Scheme 2 Synthesis of isomers **FcEt3** and **FcEt4**, **FctBu1** and **FctBu2**, **FcOhex3** and **FcOhex4**.

as confirmed by 2D HMBC measurements. Signals at δ 67 and 75 ppm were assigned to the CH_2 and CH of the pyrrolidine group, respectively, consistent with HSQC measurements. The compositions of **FcOhex1**, **FcOhex2**, **RcOhex1** and **RcOhex2** were further confirmed by elemental analysis and MALDI-TOF MS (see the Experimental section).

In addition to the 1 : 2 metallocene : [60]fullerene adducts formed in these reactions, 1 : 1 adducts were also generated as minor co-products. These 1 : 1 adducts are made by the double Prato reactions of angular di-aldehydes with fullerene.[40] In order to prepare 1 : 1 fullerene–metallocene adducts (diads) selectively, we performed two separate Prato reactions starting from the cycloaddition of mono-protected 1,1′-diformylferrocene **1** (Scheme 2). Our approach required the protection of one aldehyde group of 1,1′-diformylferrocene with 1,2-ethanedithiol to form the thioacetal **3** (Scheme 2).[42] This reaction to **3** was low yielding due to the formation of a statistical mixture of **3** and bis-thioacetal, together with unreacted dialdehyde. The protected dialdehyde **3** was reacted with fullerene in the presence of *N*-(ethyl)glycine, *N*-(4-(*tert*-butyl)benzyl)glycine (Scheme 3) or *N*-(4-(hexyloxy)benzyl)glycine to yield the thioacetals **FcS_2Et**, **FcS_2*t*Bu** and **FcS_2Ohex**, respectively (Scheme 2). These compounds are air-stable under ambient conditions and could be purified by column chromatography. The thioacetal protecting group was removed with *N*-chlorosuccinimide in the presence of $AgNO_3$ to give the organometallic fulleropyrrolidine aldehydes **FcEtAld**, **Fc*t*BuAld** and **FcOhexAld** in low to moderate yields (Scheme 2). In the final step, a dilute solution of fulleropyrrolidine aldehyde, **FcEtAld**, **Fc*t*BuAld** or **FcOhexAld**, in toluene was heated under reflux with the corresponding amino acid (Scheme 2), and in each case only two isomers of the cyclic fullerene–metallocene diad are formed. This is unusual since the addition of a second pyrrolidine group to [60]fullerene tends to give several isomers.[40,43,44] We attribute this different behaviour to the rigid structure of ferrocene restricting the number of positions to which the second pyrrolidine group can attach, thus effectively reducing the number of possible isomers to two. For each mixture the two isomers can be separated using gradient elution column chromatography on silica gel using 100% carbon disulfide → 100% toluene. For the purpose of identification, the isomers of these diad systems are labelled in the order of their elution from the column (*e.g.* **FcEt3**, **FcEt4**). Due to the relative insolubility of **FcEt3** and **FcEt4**, these products were characterised by MALDI-TOF mass spectrometry, IR and ^{1}H NMR spectroscopies only. However, the solubility of the other diad products was sufficiently high to enable more extensive characterisation. The ^{1}H NMR spectrum of each diad product exhibits one type of (alkyl)benzyl group, pyrrolidine and ferrocene moieties, and shows a very similar multiplet pattern to that of their corresponding triad compounds. In each case, MALDI-TOF mass spectrometry confirms a 1 : 1 ratio of fullerene : ferrocene in these products.



Scheme 3 Synthesis of *N*-(4-(*tert*-butyl)benzyl)glycine.

The stepwise addition of two azomethine ylides to [60]fullerene forms eight isomeric bis-adducts when a symmetric azomethine ylide is employed.[39,42] After the first pyrrolidine group is attached, the remaining [6,6]-bonds of the [60]fullerene cage are not identical and any of eight different regioisomers can be formed on addition of a second pyrrolidine (Fig. 1). The structures of these fulleropyrrolidine bis-adducts have been assigned previously by UV-vis and NMR spectroscopies with

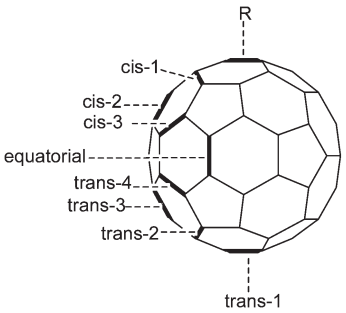


Fig. 1 Positional relationship of the eight different bonds in [60]fullerene that can react in the second step with respect to the first functional group R.

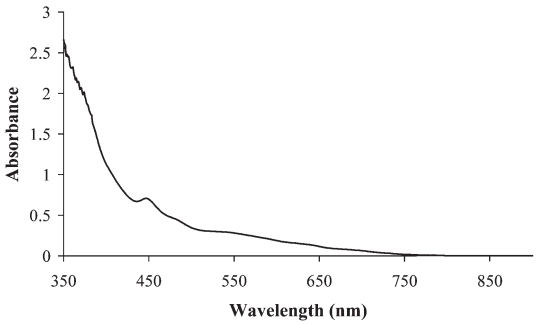


Fig. 2 UV-vis spectrum of **Fc*t*Bu1** at $C = 1.8 \times 10^{-4}$ mol L^{-1} in chloroform at 293 K.

each bis-adduct showing a unique pattern of absorption bands in the 400–750 nm region.[40,43] The number and intensity of the ^{13}C NMR signals of the residual sp^2 carbons of the fullerene cage between 130 and 160 ppm can also be used to confirm the symmetry of products.[40,43,45]

The UV-vis spectrum of **Fc*t*Bu1** suggests that the *trans*-4 isomer has been formed (Fig. 2)[43], and this is confirmed further by the observation of 32 signals (30 sp^2 fullerene-based carbon peaks) between 130 and 160 ppm in the ^{13}C NMR spectrum of this species. In the ^1H NMR spectrum, two doublets observed at δ 3.69 (^2J = 9.5 Hz) and 3.90 ppm (^2J = 9.5 Hz) are assigned to the CH_2 pyrrolidine group along with one singlet at δ 5.13 ppm corresponding to the proton at the chiral centre. The two doublets associated with the methylene adjacent to the aromatic ring were observed at δ 3.36 and 3.77 ppm (^2J = 14 Hz), and the aromatic protons appear as two doublets at 7.31 and 7.35 ppm (^3J = 8.7 Hz). The protons of the metallocene are observed as multiplets at 4.27, 4.41, 4.73 and 4.79 ppm, and the protons of the *t*Bu group appear as a singlet at 1.30 ppm. These NMR data are consistent with the expected C_s symmetry of the *trans*-4 isomer.

The UV-vis spectrum of **Fc*t*Bu2** is identical to that of **Fc*t*Bu1**. Moreover, the ^{13}C NMR spectrum of **Fc*t*Bu2** also exhibits 32 signals (30 sp^2 fullerene-based carbon peaks) between δ 130 and 160 ppm consistent with the C_s symmetry of a *trans*-4 isomer. Therefore, **Fc*t*Bu1** and **Fc*t*Bu2** are not regioisomers but are related to each other as diasteriomers due to the presence of a chiral center on each of the pyrrolidine rings. As the ^1H and ^{13}C NMR spectra of **FcOhex3**/**Fc*t*Bu1** and **FcOhex4**/**Fc*t*Bu2** exhibit similar patterns and numbers of signals, these compounds can also be assigned as *trans*-4 isomers.

Electrochemistry

The redox properties of the compounds synthesised in this study were investigated by cyclic voltammetry (CV), and electrochemical data for all the fullerene–metallocene hybrid compounds are summarised in Table 1. Reduction potentials of unfunctionalised [60]fullerene are shown in the supporting information file for comparison (ESI†). All experiments were performed in *o*-DCB containing $[N^nBu_4][BF_4]$ (0.2 M) as a supporting electrolyte at room temperature. The CV of each compound shows three consecutive reduction processes associated with fullerene moieties. The potentials of these reductions are shifted to more cathodic values compared to the parent [60]-fullerene (ESI†), consistent with the results for other functionalised [60]fullerenes.[46,47] In the case of the triad compounds, the potential for each of the three reductions did not change significantly. Thus, the nature of the metallocene and the solubilising group on the nitrogen centre of the pyrrolidine appears to have little influence upon the reduction potential of the fullerene moiety. Indeed, the reduction potentials measured for our products are virtually identical to those reported previously for other 1 : 1 fullerene–ferrocene compounds formed using Prato chemistry.[23] Fig. 3 and 4 show the cyclic voltammograms for **FcEt1** and **RcEt1**, respectively.

As expected, in addition to the three reduction processes, **FcEt1** features a reversible oxidation couple for the ferrocene moiety, while **RcEt1** shows an irreversible oxidative process. For the ferrocene triad compounds, each reductive process involved approximately double the current compared to the oxidative process, consistent with the 1 : 2 ferrocene : fullerene stoichiometry and with each of the three reduction events in the triad compounds corresponding to two-electron processes. Both [60]fullerenes in the triad compounds are reduced simultaneously suggesting no electronic communication between the fullerene cages *via* the bridging group or through space, despite the fact that the carbon cages are able to come into close proximity to each other due to the rotational freedom of the metallocene bridge and structural flexibility of pyrrolidine groups.

The oxidation potentials of the ferrocene triad complexes are more anodic than that of unmodified ferrocene indicating some depletion of electron density at the ferrocene moiety. As [60]fullerene often behaves as an electron-poor alkene, the observed higher oxidation potential of ferrocene can be attributed to an inductive electron withdrawing effect of the fullerene. The nature of the solubilising group on the pyrrolidine ring appears to have little influence on the oxidation potential of the metallocene.

The CV of cyclic diad compounds (except **FcOhex4**, which was not available in sufficient quantities for electrochemical measurements) shows three reductive and one oxidative processes. Fig. 5 shows the cyclic voltammogram of **FcEt3**. For all

Table 1 Electrochemical data[a]

Compound	E_1/V	E_{-1}/V	E_{-2}/V	E_{-3}/V	ΔE_{Fc}
FcEt1	0.16 (0.12)	−1.17 (0.15)	−1.55 (0.14)	−2.09 (0.14)	(0.12)
FcEt2	0.16 (0.10)	−1.17 (0.13)	−1.55 (0.13)	−2.09 (0.13)	(0.11)
FcOhex1	0.19 (0.11)	−1.17 (0.14)	−1.56 (0.14)	−2.10 (0.14)	(0.11)
FcOhex2	0.19 (0.11)	−1.17 (0.14)	−1.55 (0.14)	−2.09 (0.14)	(0.11)
RcEt1	0.60[b]	−1.16 (0.14)	−1.54 (0.14)	−2.09 (0.14)	(0.11)
RcEt2	0.61[b]	−1.15 (0.14)	−1.54 (0.14)	−2.09 (0.14)	(0.12)
RcOhex1	0.67[b]	−1.16 (0.14)	−1.55 (0.14)	−2.09 (0.13)	(0.12)
RcOhex2	0.67[b]	−1.16 (0.14)	−1.54 (0.13)	−2.08 (0.14)	(0.12)
FcEt3	0.14 (0.15)	−1.33 (0.15)	−1.71 (0.15)	−2.31 (0.15)	(0.10)
FcEt4	0.15 (0.11)	−1.30 (0.10)	−1.67 (0.10)	−2.29 (0.10)	(0.10)
Fc*t*Bu1	0.18 (0.11)	−1.33 (0.12)	−1.70 (0.11)	−2.30 (0.13)	(0.11)
Fc*t*Bu2	0.17 (0.10)	−1.30 (0.10)	−1.69 (0.10)	−2.29 (0.11)	(0.10)
FcOhex3	0.18 (0.11)	−1.31 (0.10)	−1.70 (0.11)	−2.30 (0.11)	(0.09)

[a] Potentials in V quoted to the nearest 0.01 V. Data reported at 0.1 V s^{-1} for 0.2 mM test solutions in 1,2-dichlorobenzene containing [^{n}Bu$_4$N][BF$_4$] (0.2 M) as supporting electrolyte. The anodic/cathodic peak separation ($\Delta E = E_p^a - E_p^c$) is given in brackets were applicable. $\Delta E_{Fc} = E_p^a - E_p^c$ for the Fc^+/Fc couple, used as the internal standard. [b] Peak anodic potential (E_p^a).

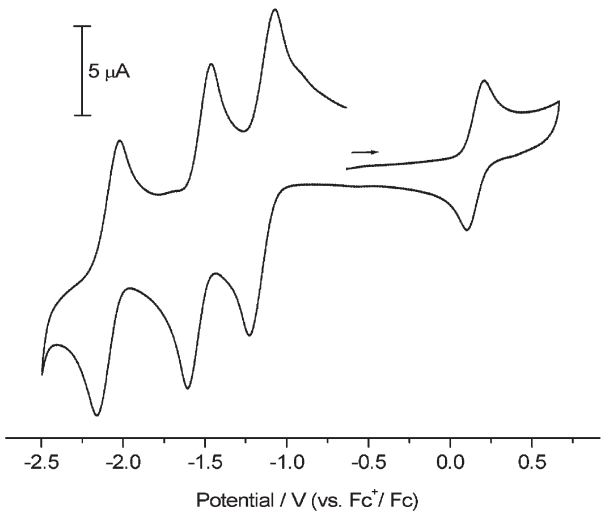


Fig. 3 Cyclic voltammogram of 0.2 mM solution of **FcEt1** in *o*-DCB containing 0.2 M [N^{n}Bu$_4$][BF$_4$] at 293 K.

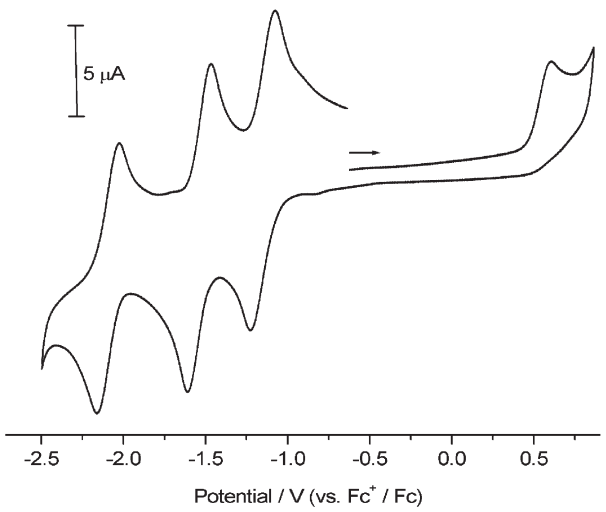


Fig. 4 Cyclic voltammogram of 0.2 mM solution of **RcEt1** in *o*-DCB containing 0.2 M [N^{n}Bu$_4$][BF$_4$] at 293 K.

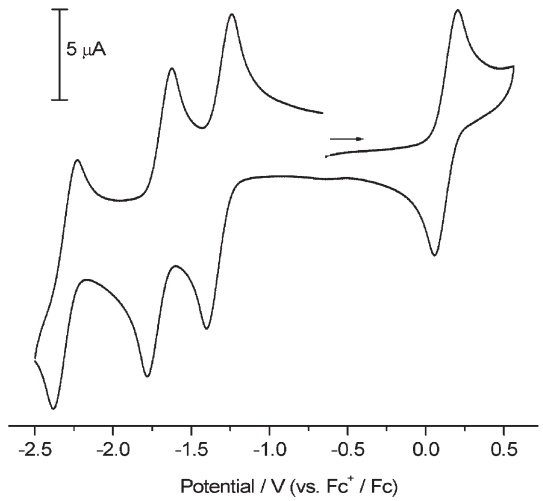
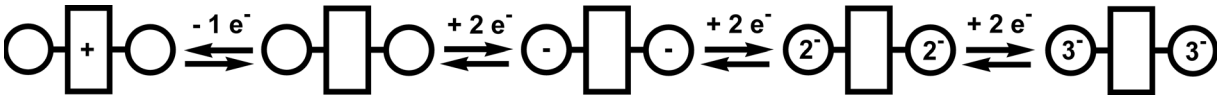
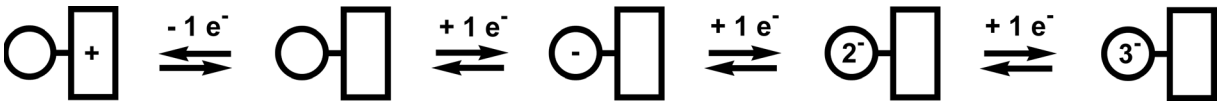


Fig. 5 Cyclic voltammogram of 0.3 mM solution of **FcEt3** in *o*-DCB containing 0.2 M [N^{n}Bu$_4$][BF$_4$] at 293 K.

of these compounds, the reduction wave for the [60]fullerene moiety has a similar current peak height to that of the oxidative wave of the ferrocene unit. This is consistent with each of the three reduction waves corresponding to one-electron processes. The potentials of the three reductive processes in the cyclic diad compounds are shifted cathodically relative to free [60]fullerene and the triad complexes. This results from an increase in the energy of the LUMO due to the functionalisation of fullerene cage, consistent with previous reports that the HOMO–LUMO gap of [60]fullerenes increases with the number of functional groups.[48–50] Conversely, the oxidation potentials for the cyclic diad compounds are very similar to those for the triad compounds, indicating that the metallocene moiety has similar electronic properties in each system. This is consistent with the similar nature of cyclopentadienyl substitution in both diad and triad compounds. A summary of the trends of the redox chemistry for these complexes is given in Schemes 4 and 5.



Scheme 4 Distribution of electrons in the triad compounds. The individual acceptor ([60]fullerene) and donor (ferrocene or ruthenocene) units are represented by a circle and a rectangle, respectively.



Scheme 5 Distribution of electrons into the diad compounds. The individual acceptor ([60]fullerene) and donor (ferrocene) units are represented by a circle and a rectangle, respectively.

Conclusions

We have demonstrated that metallocene bis-aldehydes react efficiently with [60]fullerene in 1 : 2 or 1 : 1 ratios to form triad (fullerene–metallocene–fullerene) or diad (fullerene–metallocene) compounds, respectively. Both types of compounds are formed as mixtures of diastereomers which can be separated by column chromatography. All cyclic diad compounds correspond exclusively to one regioisomer, the 4-*trans* isomer as revealed by spectroscopic studies. All compounds exhibit rich redox behaviour, with the fullerene and metallocene moieties acting as electron acceptors and donors, respectively. The triad compounds accept up to six electrons, added as three pairs – one per fullerene cage for each of three reduction steps. In contrast, the diad complexes are able to accept three electrons individually, one in each of the fullerene reduction processes. Both diads and triads exhibit oxidations associated with the metallocene moiety. Linking one (or two) [60]fullerene groups to a metallocene alters the redox potential of each constituent part as compared to [60]fullerene and the metallocene. The control of structure, composition and physical properties (solubility) of donor–acceptor systems and the tuning of their electrochemical properties demonstrated in this study may form a basis for exploitation of organometallic derivatives of fullerenes in photovoltaic and electronic devices.

Experimental

All reagents were purchased from commercial suppliers (Aldrich, Acros, Lancaster and Fluka) and were used as received. Ar and N_2 were obtained as high-purity gases from BOC gases. Silica gel was purchased from Fluorochem (35–70 microns). All solvents were pre-dried as required; CH_2Cl_2 was distilled under N_2 over CaH_2. Toluene, diethyl ether and iso-hexane were dried using Grubbs drying systems. Tetrahydrofuran was distilled from sodium/sodium benzophenone under N_2. Isopropanol was dried over Mg/I_2 and distilled prior to use. Dicyclopentadiene was heated at 200 °C with iron powder and cyclopentadiene was collected by distillation. TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was distilled over sodium and water was purified (>18 ΩM cm) using a Barnstead NANOPure II system.

IR spectra were measured in solid state over the range 400–4000 cm^{-1} using a Bruker Tenser 27 FT-IR spectrometer equipped with a Pike Technologies MIRacle ATR attachment. NMR spectra were recorded on either a Bruker DPX300 (300.13 MHz), DPX400 (400.20 MHz), AV400 (400.20 MHz), AV(III)400 (400.20 MHz) or AV(III)500 (500.13 MHz) spectrometer 300 K. Mass spectrometric data were recorded by the Mass Spectrometry Service Centre at the University of Nottingham on a Bruker Ultraflex III instrument. All MALDI-TOF measurements were conducted in negative mode using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile) as the matrix. UV-vis spectra were recorded in solution using 1 cm quartz cuvettes using a Perkin-Elmer Lambda 25 UV-vis spectrophotometer at a scan rate of 240 nm min^{-1} over the range of 190–900 nm, and extinction coefficients (ε) are quoted in units of $dm^3\ mol^{-1}\ cm^{-1}$, unless otherwise stated. Elemental analyses were carried out by the Microanalysis Service at the University of Nottingham (Exeter Analytical Inc. CE-440 Elemental Analyser) or at the London Metropolitan University (Carlo Erba CE1108 Elemental Analyser). Electrochemical samples (2 or 3 mM) were dissolved in *o*-DCB containing 0.2 M $[N^nBu_4][BF_4]$ as the supporting electrolyte. Cyclic voltammograms were recorded in a series of scan-rates (ν) (typically ν = 0.02–0.3 V s^{-1}) using an Eco Chemie Autolab PGSTAT20 potentiostat and reported against ferrocene ($FeCp_2/[FeCp_2]^+$ = +0.00 V). For the ferrocene derivatives, the $[FeCp_2^*]^+/[FeCp_2^*]$ couple was used as the internal reference to avoid overlap between the oxidation couple for the compound and the internal standard. Under these circumstances the potentials of the redox processes were referenced to that of the Fc^+/Fc couple by an independent calibration. The $\Delta E_{1/2}$ between Fc^+/Fc and $[FeCp_2^*]^+/[FeCp_2^*]$ recorded under identical conditions was 0.52 V. Cyclic voltammetry was performed in a single compartment cell using a glassy carbon working electrode, a Pt wire secondary electrode and a saturated calomel reference electrode.

The following compounds were synthesised by literature procedures, ruthenocene,[51] 1,1′-diformylferrocene **1** and 1,1′-diformylruthenocene **2**[52–54] and 1-[2-(1,3-dithiolanyl)]-1′-formylferrocene **3**.[42] *N*-(4-(hexyloxy)benzyl)glycine was synthesised

using the reported method,[39] and *N*-(ethyl)glycine was purchased commercially.

Synthesis of methyl 2-(4-(*tert*-butyl)benzylamino)acetate 4

To a solution of 4-(*tert*-butyl)benzaldehyde (4.1 mL, 24.6 mmol) in CH_2Cl_2 (200 mL) was added the hydrochloride salt of the glycine ester (3.88 g, 30.9 mmol), triethylamine (4.3 mL, 30.8 mmol) and a small quantity of molecular sieves 4 Å (*ca*. 2 g) and the reaction mixture was stirred at r.t. for 17 h. The reaction mixture was filtered and the solvent removed *in vacuo*. To a solution of this residue in MeOH (20 mL) at 0 °C was added $NaBH_4$ (1.17 g, 30.9 mmol) and the mixture stirred at 0 °C for 30 min. After the addition of a saturated solution of $NaHCO_3$ (60 mL), the mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 7 : 3 as the eluent to yield **4** as a yellow oil (3.35 g, 59%). NMR (MeOD): ^{1}H (400 MHz), δ 1.31 (s, 9H, C(CH_3)$_3$), 3.36 (s, 2H, NHCH_2CO$_2$Me), 3.71 (s, 3H, Me), 3.72 (s, 2H, NHCH_2Ph*t*Bu), 7.24 (d, ^3J = 8.33 Hz, 2H, aromatic C*H* close to NHCH$_2$CO$_2$Me), 7.36 (d, ^3J = 8.33 Hz, 2H, aromatic C*H* close to Bn*t*Bu); ^{13}C (100 MHz), δ 31.94 (C(*C*H$_3$)$_3$), 35.45 (*C*(CH$_3$)$_3$), 50.09 (Me), 52.37 (NH*C*H$_2$CO$_2$Me), 53.55 (NH*C*H$_2$Ph*t*Bu), 126.53 (aromatic *C*H close to Bn*t*Bu), 129.54 (aromatic *C*H close to NHCH$_2$CO$_2$Me), 137.13 (aromatic *Cq* close to NHCH$_2$CO$_2$Me), 151.55 (aromatic *Cq* close to Bn*t*Bu), 173.82 (*C*OOMe). MS (ESI$^+$, MeOH) *m*/*z* 236 [M + H]$^+$.

Synthesis of *N*-(4-(*tert*-butyl)benzyl)glycine 5

A solution of NaOH (568.4 mg, 14.2 mmol) and ester **4** (3.35 g, 14.2 mmol) in MeOH (25 mL) was stirred at r.t. for 17 h. The solvent was then removed *in vacuo*, and after the addition of water (20 mL), the pH of the solution was adjusted to 6.7 with a solution of 2 M HCl. The white precipitate was separated by filtration, and washed with water and Et_2O to yield **5** as a white solid (2.91 g, 93%). NMR (MeOD): ^{1}H (400 MHz), δ 1.30 (s, 9H, C(CH_3)$_3$), 3.61 (s, 2H, NHCH_2CO$_2$H), 4.17 (s, 2H, NHCH_2Ph*t*Bu), 7.38 (d, ^3J = 8.48 Hz, 2H, aromatic C*H* close to NHCH$_2$CO$_2$H), 7.46 (d, ^3J = 8.48 Hz, 2H, aromatic C*H* close to Bn*t*Bu); ^{13}C (100 MHz), δ 31.77 (C(*C*H$_3$)$_3$), 35.73 (*C*(CH$_3$)$_3$), 48.97 (NH*C*H$_2$CO$_2$H), 51.73 (NH*C*H$_2$Ph*t*Bu), 127.35 (aromatic *C*H close to Bn*t*Bu), 129.69 (aromatic *Cq* close to NHCH$_2$CO$_2$H), 130.95 (aromatic *C*H close to NHCH$_2$CO$_2$H), 154.18 (aromatic *Cq* close to Bn*t*Bu), 170.16 (carboxylic acid). MS (ESI$^+$, MeOH) *m*/*z* 222 [M + H]$^+$.

Synthesis of FcEt1 and FcEt2

A solution of [60]fullerene (121.3 mg, 0.168 mmol), *N*-(ethyl)-glycine (21.7 mg, 0.210 mmol) and 1,1′-diformylferrocene **1** (12.0 mg, 0.050 mmol) in dry toluene (100 mL) was heated under reflux for 17 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcEt1** (20.1 mg, 23%) and **FcEt2** (17.5 mg, 20%), as brown solids.

For FcEt1. R_f (carbon disulfide : toluene 10%) 0.55. NMR (CDCl$_3$/CS$_2$ 30%): ^{1}H (400 MHz), δ 1.84 (t, ^3J = 6.95 Hz, 6H, NHCH$_2$CH_3), 3.06 (m, 2H, NHCH_2CH$_3$), 4.16 (d, ^2J = 9.7 Hz, 2H, CH_2 pyrrolidine), 4.40 (br s, 4H, C*H* Cp ring), 4.60 (br s, 2H, C*H* Cp ring), 4.71 (br s, 2H, C*H* Cp ring), 4.90 (m, 2H, NHCH_2CH$_3$), 5.04 (s, 2H, C*H* pyrrolidine), 5.14 (d, ^2J = 9.7 Hz, 2H, CH_2 pyrrolidine) (Found: C, 93.99; H, 1.26; N, 1.52. $C_{138}H_{24}N_2Fe$ requires C, 93.88; H, 1.37; N, 1.59%). IR: 2961w, 2785w (ν_{C-H}), 1512m, 1462m, 1427m, 1382m ($\nu_{C=C}$), 1316m, 1190m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1765 [M]$^-$.

For FcEt2. R_f (carbon disulfide : toluene 10%) 0.29. NMR (CDCl$_3$/CS$_2$ 30%): ^{1}H (400 MHz), δ 1.81 (t, ^3J = 7.0 Hz, 6H, NHCH$_2$CH_3), 3.02 (m, 2H, NHCH_2CH$_3$), 4.16 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 4.38 (br s, 2H, C*H* Cp ring), 4.43 (br s, 2H, C*H* Cp ring), 4.59 (br s, 2H, C*H* Cp ring), 4.67 (br s, 2H, C*H* Cp ring), 4.97 (m, 2H, NHCH_2CH$_3$), 5.08 (s, 2H, C*H* pyrrolidine), 5.13 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine) (Found: C, 93.74; H, 1.25; N, 1.54. $C_{138}H_{24}N_2Fe$ requires C, 93.88; H, 1.37; N, 1.59%). IR: 2963w, 2810w (ν_{C-H}), 1512m, 1463m, 1429m, 1382m ($\nu_{C=C}$), 1316m, 1189m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1765 [M]$^-$.

Synthesis of RcEt1 and RcEt2

A solution of [60]fullerene (121.5 mg, 0.169 mmol), *N*-(ethyl)-glycine (22.5 mg, 0.218 mmol) and 1,1′-diformylruthenocene **2** (10.0 mg, 0.035 mmol) in dry toluene (100 mL) was heated under reflux for 17 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **RcEt1** (18.2 mg, 27%) and **RcEt2** (13.9 mg, 22%), as brown solids.

For RcEt1. R_f (carbon disulfide : toluene 10%) 0.56. NMR (CDCl$_3$/CS$_2$ 30%): ^{1}H (400 MHz), δ 1.72 (t, ^3J = 7.2 Hz, 6H, NHCH$_2$CH_3), 2.79 (m, 2H, NHCH_2CH$_3$), 4.09 (d, ^2J = 9.2 Hz, 2H, CH_2 pyrrolidine), 4.68 (br s, 6H, C*H* Cp ring + NHCH_2CH$_3$), 4.86 (br s, 2H, C*H* Cp ring), 4.95 (br s, 2H, C*H* Cp ring), 5.10 (d, ^2J = 9.2 Hz, 2H, CH_2 pyrrolidine), 5.16 (s, 2H, C*H* pyrrolidine). IR: 2968w, 2806w (ν_{C-H}), 1512m, 1462m, 1429m, 1383m ($\nu_{C=C}$), 1316m, 1188m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1811 [M]$^-$.

For RcEt2. R_f (carbon disulfide : toluene 10%) 0.32. NMR (CDCl$_3$/CS$_2$ 30%): ^{1}H (400 MHz), δ 1.68 (t, ^3J = 7.0 Hz, 6H, NHCH$_2$CH_3), 2.73 (m, 2H, NHCH_2CH$_3$), 4.08 (d, ^2J = 9.1 Hz, 2H, CH_2 pyrrolidine), 4.65 (br s, 4H, C*H* Cp ring + NHCH_2CH$_3$), 4.71 (br s, 2H, C*H* Cp ring), 4.88 (br s, 2H, C*H* Cp ring), 4.96 (br s, 2H, C*H* Cp ring), 5.08 (d, ^2J = 9.1 Hz, 2H, CH_2 pyrrolidine), 5.16 (s, 2H, C*H* pyrrolidine). IR: 2965w, 2860w (ν_{C-H}), 1513m, 1462m, 1429m, 1382m ($\nu_{C=C}$), 1316m, 1188m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1811 [M]$^-$.

Synthesis of FcOhex1 and FcOhex2

A solution of [60]fullerene (100.3 mg, 0.139 mmol), *N*-(4-(hexyloxy)benzyl)glycine (17.9 mg, 0.174 mmol) and 1,1′-diformylferrocene **1** (10.1 mg, 0.042 mmol) in dry toluene (100 mL) was heated under reflux for 17 h under Ar. The solvent was removed from the cooled solution *in vacuo* and the crude

residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcOhex1** (18.4 mg, 21%) and **FcOhex2** (16.5 mg, 19%) as brown solids.

For FcOhex1. R_f (carbon disulfide : toluene 7%) 0.48. NMR ($CDCl_3$): ^1H (500 MHz), δ 0.88 (t, ^3J = 6.6 Hz, 6H, CH_3 alkyl chain), 1.35 (m, 8H, CH_2 alkyl chain), 1.51 (m, 4H, CH_2 alkyl chain), 1.84 (m, 4H, BnOCH$_2$CH_2), 3.70 (d, ^2J = 13.1 Hz, 2H, NHCH_2PhOhexyl), 3.88 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 4.06 (t, ^3J = 6.6 Hz, 4H, BnOCH_2), 4.38 (br s, 2H, C*H* Cp ring), 4.46 (br s, 2H, C*H* Cp ring), 4.68 (br s, 2H, C*H* Cp ring), 4.75 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 4.85 (br s, 2H, C*H* Cp ring), 5.10 (s, 2H, C*H* pyrrolidine), 6.39 (d, ^2J = 13.1 Hz, 2H, NHCH_2PhOhexyl), 7.18 (d, ^3J = 8.5 Hz, 4H, aromatic C*H* BnOhexyl), 7.83 (d, ^3J = 8.5 Hz, 4H, aromatic C*H* BnOhexyl);.^{13}C (125 MHz), δ 14.06 (*C*H$_3$ alkyl chain), 22.62 (*C*H$_2$ alkyl chain), 25.80 (*C*H$_2$ alkyl chain), 29.30 (*C*H$_2$ alkyl chain), 31.62 (*C*H$_2$ alkyl chain), 57.93 (NH*C*H$_2$PhOhexyl), 67.59 (*C*H$_2$ pyrrolidine), 67.98 (BnO*C*H$_2$), 68.23 (*C* attached to C_{60}), 68.44 (*C*H Cp ring), 68.63 (*C*H Cp ring), 68.73 (*C*H Cp ring), 69.57 (*C*H Cp ring), 74.90 (*C*H pyrrolidine), 77.88 (*C* attached to C_{60}), 87.81 (*Cq* Cp ring), 115.10 (aromatic *C*H BnOhexyl), 129.52 (aromatic *C*H BnOhexyl), 131.15–158.77 (C_{60} and quaternary aromatic carbons) (Found: C, 91.99; H, 2.40; N, 1.30. $C_{160}H_{52}N_2O_2Fe$ requires C, 91.95; H, 2.51; N, 1.34%). IR: 2924w, 2853w (ν_{C-H}), 1610w, 1510m, 1463m, 1431m, 1376m ($\nu_{C=C}$), 1245m, 1170m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 2089 [M]$^-$.

For FcOhex2. R_f (carbon disulfide : toluene 7%) 0.22. NMR ($CDCl_3$): ^1H (500 MHz), δ 0.89 (t, ^3J = 6.6 Hz, 6H, CH_3 alkyl chain), 1.40 (m, 8H, CH_2 alkyl chain), 1.55 (m, 4H, CH_2 alkyl chain), 1.86 (m, 4H, BnOCH$_2$CH_2), 3.78 (d, ^2J = 12.5 Hz, 2H, NHCH_2PhOhexyl), 4.07 (t, ^3J = 6.6 Hz, 4H, BnOCH_2), 4.11 (d, ^2J = 9.6 Hz, 2H, CH_2 pyrrolidine), 4.49 (br s, 2H, C*H* Cp ring), 4.51 (br s, 2H, C*H* Cp ring), 4.70 (br s, 2H, C*H* Cp ring), 4.73 (d, ^2J = 9.6 Hz, 2H, CH_2 pyrrolidine), 4.85 (br s, 2H, C*H* Cp ring), 5.20 (s, 2H, C*H* pyrrolidine), 6.23 (d, ^2J = 12.5 Hz, 2H, NHCH_2PhOhexyl), 7.02 (d, ^3J = 8.5 Hz, 4H, aromatic C*H* BnOhexyl), 7.64 (d, ^3J = 8.5 Hz, 4H, aromatic C*H* BnOhexyl); ^{13}C (125 MHz), δ 14.09 (*C*H$_3$ alkyl chain), 22.66 (*C*H$_2$ alkyl chain), 25.87 (*C*H$_2$ alkyl chain), 29.69 (*C*H$_2$ alkyl chain), 31.70 (*C*H$_2$ alkyl chain), 57.99 (NH*C*H$_2$PhOhexyl), 67.59 (*C*H$_2$ pyrrolidine), 67.98 (BnO*C*H$_2$), 68.22 (*C* attached to C_{60}), 68.89 (*C*H Cp ring), 68.96 (*C*H Cp ring), 69.62 (*C*H Cp ring), 71.23 (*C*H Cp ring), 75.10 (*C*H pyrrolidine), 78.01 (*C* attached to C_{60}), 87.85 (*Cq* Cp ring), 114.87 (aromatic *C*H BnOhexyl), 129.86 (aromatic *C*H BnOhexyl), 132.54–158.52 (C_{60} and quaternary aromatic carbons) (Found: C, 91.87; H, 2.39; N, 1.31. $C_{160}H_{52}N_2O_2Fe$ requires C, 91.95; H, 2.51; N, 1.34%). IR: 2924w, 2851w (ν_{C-H}), 1610w, 1510m, 1465m, 1431m, 1378m ($\nu_{C=C}$), 1245m, 1170m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 2089 [M]$^-$.

Synthesis of RcOhex1 and RcOhex2

A solution of [60]fullerene (102.3 mg, 0.142 mmol), *N*-(4-(hexyloxy)benzyl)glycine (51.1 mg, 0.183 mmol) and 1,1′-diformylruthenocene **2** (8.6 mg, 0.030 mmol) in dry toluene (100 mL) was heated under reflux for 17 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **RcOhex1** (14.7 mg, 23%) and **RcOhex2** (12.8 mg, 20%) as brown solids.

For RcOhex1. R_f (carbon disulfide : toluene 7%) 0.50. NMR ($CDCl_3$): ^1H (500 MHz), δ 0.90 (t, ^3J = 6.9 Hz, 6H, CH_3 alkyl chain), 1.34 (m, 8H, CH_2 alkyl chain), 1.36 (m, 4H, CH_2 alkyl chain), 1.82 (m, 4H, BnOCH$_2$CH_2), 3.46 (d, ^2J = 13.1 Hz, 2H, NHCH_2PhOhexyl), 3.78 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 4.04 (t, ^3J = 6.6 Hz, 4H, BnOCH_2), 4.69 (br s, 2H, C*H* Cp ring), 4.74 (s, 4H, CH_2 pyrrolidine + C*H* Cp ring), 4.89 (s, 2H, C*H* pyrrolidine), 5.02 (br s, 2H, C*H* Cp ring), 5.30 (br s, 2H, C*H* Cp ring), 6.12 (d, ^2J = 13.1 Hz, 2H, NHCH_2PhOhexyl), 7.13 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl), 7.75 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl); ^{13}C (125 MHz), δ 14.07 (*C*H$_3$ alkyl chain), 22.63 (*C*H$_2$ alkyl chain), 25.79 (*C*H$_2$ alkyl chain), 29.29 (*C*H$_2$ alkyl chain), 31.60 (*C*H$_2$ alkyl chain), 58.30 (NH*C*H$_2$PhOhexyl), 67.78 (*C*H$_2$ pyrrolidine), 67.85 (*C*H Cp ring), 67.93 (BnO*C*H$_2$), 68.20 (*C* attached to C_{60}), 70.89 (*C*H Cp ring), 71.49 (*C*H Cp ring), 72.25 (CH Cp ring), 72.54 (*C*H Cp ring), 74.66 (*C*H pyrrolidine), 77.92 (*C* attached to C_{60}), 91.35 (*Cq* Cp ring), 115.05 (aromatic *C*H BnOhexyl), 129.46 (aromatic *C*H BnOhexyl), 130.52–158.67 (C_{60} and quaternary aromatic carbons) (Found: C, 89.96; H, 2.40; N, 1.31. $C_{160}H_{52}N_2O_2Ru$ requires C, 90.00; H, 2.45; N, 1.31%). IR: 2926w, 2855w (ν_{C-H}), 1611w, 1510m, 1464m, 1430m, 1376m ($\nu_{C=C}$), 1244m, 1170m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 2136 [M]$^-$.

For RcOhex2. R_f (carbon disulfide : toluene 7%) 0.24. NMR ($CDCl_3$): ^1H (500 MHz), δ 0.93 (t, ^3J = 7.1 Hz, 6H, CH_3 alkyl chain), 1.38 (m, 8H, CH_2 alkyl chain), 1.52 (m, 4H, CH_2 alkyl chain), 1.85 (m, 4H, BnOCH$_2$CH_2), 3.53 (d, ^2J = 12.6 Hz, 2H, NHCH_2PhOhexyl), 4.04 (m, 6H, CH_2 pyrrolidine + BnOCH_2), 4.74 (s, 6H, CH_2 pyrrolidine + C*H* Cp ring), 5.02 (s, 2H, C*H* pyrrolidine), 5.06 (br s, 2H, C*H* Cp ring), 5.30 (br s, 2H, C*H* Cp ring), 5.91 (d, ^2J = 12.6 Hz, 2H, NHCH_2PhOhexyl), 7.01 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl), 7.59 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl); ^{13}C (125 MHz), δ 14.08 (*C*H$_3$ alkyl chain), 22.64 (*C*H$_2$ alkyl chain), 25.83 (*C*H$_2$ alkyl chain), 29.41 (*C*H$_2$ alkyl chain), 31.66 (*C*H$_2$ alkyl chain), 58.36 (NH*C*H$_2$PhOhexyl), 67.90 (*C*H$_2$ pyrrolidine), 68.07 (BnO*C*H$_2$), 68.20 (*C* attached to C_{60}), 71.33 (*C*H Cp ring), 71.79 (*C*H Cp ring), 73.53 (*C*H Cp ring), 72.54 (*C*H Cp ring), 75.46 (*C*H pyrrolidine), 78.03 (*C* attached to C_{60}), 91.20 (*Cq* Cp ring), 114.81 (aromatic *C*H BnOhexyl), 129.70 (aromatic *C*H BnOhexyl), 130.52–158.54 (C_{60} and quaternary aromatic carbons). IR: 2926w, 2853w (ν_{C-H}), 1610w, 1510m, 1464m, 1430m, 1375m ($\nu_{C=C}$), 1243m, 1170m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 2136 [M]$^-$.

Synthesis of FcS_2Et

A solution of [60]fullerene (101.7 mg, 0.141 mmol), *N*-(ethyl)-glycine (72.4 mg, 0.709 mmol) and 1-[2-(1,3-dithiolanyl)]-1′-formylferrocene **3** (54.2 mg, 0.170 mmol) in dry toluene (150 mL) was heated under reflux for 15 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcS_2Et** as a brown solid

(79.4 mg, 52%). NMR ($CDCl_3$): ^{1}H (500 MHz), δ 1.69 (t, ^3J = 7.3 Hz, 3H, NHCH$_2$C*H*$_3$), 2.99 (m, 1H, NHC*H*$_2$CH$_3$), 3.32 (m, 2H, SC*H*$_2$C*H*$_2$S), 3.44 (m, 2H, SC*H*$_2$C*H*$_2$S), 4.12 (d, ^2J = 9.5 Hz, 1H, C*H*$_2$ pyrrolidine), 4.29 (m, 1H, C*H* Cp ring), 4.31 (m, 2H, C*H* Cp ring), 4.34 (m, 1H, C*H* Cp ring), 4.44 (m, 1H, C*H* Cp ring), 4.47 (m, 1H, C*H* Cp ring), 4.52 (m, 1H, C*H* Cp ring), 4.60 (m, 1H, C*H* Cp ring), 4.68 (m, 1H, NHC*H*$_2$CH$_3$), 5.03 (s, 1H, C*H* pyrrolidine), 5.04 (d, ^2J = 9.5 Hz, 1H, C*H*$_2$ pyrrolidine), 5.66 (s, 1H, CpC*H*S$_2$Et$_2$); ^{13}C (125 MHz), δ 14.12 (NHCH$_2$*C*H$_3$), 39.92 (S*C*H$_2$*C*H$_2$S), 48.19 (N*C*H$_2$CH$_3$), 52.92 (Cp*C*HS$_2$Et$_2$), 67.05 (*C*H$_2$ pyrrolidine), 67.61 (*C*H Cp ring), 68.43 (*C* attached to C_{60}), 69.03 (*C*H Cp ring), 69.13 (*C*H Cp ring), 69.43 (*C*H Cp ring), 70.06 (*C*H Cp ring), 70.08 (*C*H Cp ring), 76.06 (*C*H pyrrolidine), 78.08 (*C* attached to C_{60}), 87.89 (*Cq* Cp ring), 89.31 (*Cq* Cp ring), 135.72–156.47 (C_{60} and quaternary aromatic carbons). IR: 2918w, 2802w (ν_{C-H}), 1463m, 1429m, 1383m, 1339m ($\nu_{C=C}$), 1264m, 1188m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1080 [M]$^-$.

Synthesis of FcS$_2$*t*Bu

A solution of [60]fullerene (101.7 mg, 0.141 mmol), *N*-(4-(*tert*-butyl)benzyl)glycine **5** (155.4 mg, 0.703 mmol) and 1-[2-(1,3-dithiolanyl)]-1′-formylferrocene **3** (54.2 mg, 0.170 mmol) in dry toluene (150 mL) was heated under reflux for 15 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcS$_2$*t*Bu** as a brown solid (83.7 mg, 50%). NMR ($CDCl_3$): ^{1}H (500 MHz), δ 1.43 (s, 9H, C(C*H*$_3$)$_3$), 3.30 (m, 2H, SC*H*$_2$C*H*$_2$S), 3.43 (m, 2H, SC*H*$_2$C*H*$_2$S), 3.82 (d, ^2J = 13.1 Hz, 1H, NHC*H*$_2$Ph*t*Bu), 4.11 (d, ^2J = 9.6 Hz, 1H, C*H*$_2$ pyrrolidine), 4.33 (m, 4H, C*H* Cp ring), 4.42 (m, 1H, C*H* Cp ring), 4.52 (m, 1H, C*H* Cp ring), 4.59 (m, 1H, C*H* Cp ring), 4.73 (m, 1H, C*H* Cp ring), 4.81 (d, ^2J = 9.6 Hz, 1H, C*H*$_2$ pyrrolidine), 5.20 (s, 1H, C*H* pyrrolidine), 5.64 (s, 1H, CpC*H*S$_2$Et$_2$), 6.11 (d, ^2J = 13.1 Hz, 1H, NHC*H*$_2$Ph*t*Bu), 7.57 (d, ^3J = 8.5 Hz, 2H, aromatic C*H* Bn*t*Bu), 7.77 (d, ^3J = 8.5 Hz, 2H, aromatic C*H* Bn*t*Bu); ^{13}C (125 MHz), δ 31.51 (C(*C*H$_3$)$_3$), 34.64 (*C*(CH$_3$)$_3$), 39.84 (S*C*H$_2$*C*H$_2$S), 52.90 (Cp*C*HS$_2$Et$_2$), 57.94 (NH*C*H$_2$Ph*t*Bu), 67.62 (*C*H Cp ring), 67.68 (*C*H$_2$ pyrrolidine), 68.42 (*C* attached to C_{60}), 68.44 (*C*H Cp ring), 69.19 (*C*H Cp ring), 69.24 (*C*H Cp ring), 69.43 (*C*H Cp ring), 70.10 (*C*H Cp ring), 70.18 (*C*H Cp ring), 75.73 (*C*H pyrrolidine), 78.05 (*C* attached to C_{60}), 87.58 (*Cq* Cp ring), 89.40 (*Cq* Cp ring), 125.79 (aromatic *C*H Bn*t*Bu), 128.05 (aromatic *C*H Bn*t*Bu), 135.71–156.41 (C_{60} and quaternary aromatic carbons). IR (solid): 2955w, 2919w, 2854w, 2800w (ν_{C-H}), 1512m, 1463m, 1429m, 1398m, 1338m ($\nu_{C=C}$), 1267m, 1184m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1200 [M]$^-$.

Synthesis of FcS$_2$Ohex

A solution of [60]fullerene (101.8 mg, 0.141 mmol), *N*-(4-(hexyloxy)benzyl)glycine (181.8 mg, 0.685 mmol) and 1-[2-(1,3-dithiolanyl)]-1′-formylferrocene **3** (56.0 mg, 0.176 mmol) in dry toluene (150 mL) was heated under reflux for 15 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcS$_2$Ohex** as a brown solid (93.0 mg, 53%). NMR ($CDCl_3$): ^{1}H (500 MHz), δ 0.94 (t, ^3J = 6.6 Hz, 3H, C*H*$_3$ alkyl chain), 1.39 (m, 4H, C*H*$_2$ alkyl chain), 1.52 (m, 2H, C*H*$_2$ alkyl chain), 1.85 (m, 2H, BnOCH$_2$C*H*$_2$), 3.30 (br s, 2H, SC*H*$_2$C*H*$_2$S), 3.43 (br s, 2H, SC*H*$_2$C*H*$_2$S), 3.79 (br s, 1H, NHC*H*$_2$PhOhexyl), 4.05 (br s, 2H, BnOC*H*$_2$), 4.11 (br s, 1H, pyrrolidine), 4.33 (br s, 4H, C*H* Cp ring), 4.43 (br s, 1H, C*H* Cp ring), 4.51 (br s, 1H, C*H* Cp ring), 4.57 (br s, 1H, C*H* Cp ring), 4.76 (br s, 2H, C*H*$_2$ pyrrolidine + C*H* Cp ring), 5.17 (s, 1H, C*H* pyrrolidine), 5.63 (s, 1H, CpC*H*S$_2$Et$_2$), 6.04 (br s, 1H, NHC*H*$_2$PhOhexyl), 7.08 (br s, 2H, aromatic C*H* BnOhexyl), 7.74 (br s, 2H, aromatic C*H* BnOhexyl); ^{13}C (125 MHz), δ 14.07 (*C*H$_3$ alkyl chain), 22.61 (*C*H$_2$ alkyl chain), 25.79 (*C*H$_2$ alkyl chain), 29.32 (*C*H$_2$ alkyl chain), 31.60 (*C*H$_2$ alkyl chain), 39.89 (S*C*H$_2$*C*H$_2$S), 52.92 (Cp*C*HS$_2$Et$_2$), 57.80 (NH*C*H$_2$PhOhexyl), 67.50 (*C*H$_2$ pyrrolidine), 67.64 (*C*H Cp ring), 68.09 (BnO*C*H$_2$), 68.20 (*C* attached to C_{60}), 68.55 (*C*H Cp ring), 69.15 (*C*H Cp ring), 69.28 (*C*H Cp ring), 69.56 (*C*H Cp ring), 70.12 (*C*H Cp ring), 70.15 (*C*H Cp ring), 75.60 (*C*H pyrrolidine), 77.97 (*C* attached to C_{60}), 87.44 (*Cq* Cp ring), 89.37 (*Cq* Cp ring), 114.81 (aromatic *C*H BnOhexyl), 129.64 (aromatic *C*H BnOhexyl), 135.72–158.60 (C_{60} and quaternary aromatic carbons) (Found: C, 84.94; H, 2.76; N, 1.08. $C_{88}H_{35}NOFeS_2$ requires C, 85.09; H, 2.84; N, 1.13%). IR: 2960w, 2917w, 2866w, 2784w (ν_{C-H}), 1611m, 1510m, 1463m, 1428m, 1383m, 1339m ($\nu_{C=C}$), 1260m, 1170m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1242 [M]$^-$.

Synthesis of FcEtAld

To a solution of *N*-chlorosuccinimide (64.8 mg, 0.485 mmol) and $AgNO_3$ (62.7 mg, 0.369 mmol) in acetonitrile : water 85 : 15 (35 mL) was added rapidly a solution of **FcS$_2$Et** (53.4 mg, 0.049 mmol) in tetrahydrofuran (THF) (50 mL) and the dark suspension stirred at r.t. for 4 h. To this solution was added a saturated solution of Na_2SO_3 (1 mL) and a saturated solution of $NaHCO_3$ (2 mL) and then brine (1 mL) at 1 min intervals. After the addition of CH_2Cl_2 (50 mL), the mixture was stirred at r.t. for 15 min and the resulting two layers were separated and the organic phase washed with water. The organic layers were combined and passed through a pad of cotton wool. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from toluene to ethyl acetate was used to yield **FcEtAld** as a brown solid (14.3 mg, 29%). NMR ($CDCl_3$): ^{1}H (500 MHz), δ 1.69 (t, ^3J = 7.3 Hz, 3H, NHCH$_2$C*H*$_3$), 2.99 (m, 1H, NHC*H*$_2$CH$_3$), 4.11 (d, ^2J = 9.5 Hz, 1H, C*H*$_2$ pyrrolidine), 4.35 (m, 1H, C*H* Cp ring), 4.38 (m, 1H, C*H* Cp ring), 4.57 (m, 1H, NHC*H*$_2$CH$_3$), 4.62 (m, 1H, C*H* Cp ring), 4.68 (m, 1H, C*H* Cp ring), 4.74 (m, 1H, C*H* Cp ring), 4.76 (m, 1H, C*H* Cp ring), 4.92 (m, 3H, C*H* Cp ring + C*H* pyrrolidine), 5.04 (d, ^2J = 9.5 Hz, 1H, C*H*$_2$ pyrrolidine), 10.08 (s, 1H, aldehyde); ^{13}C (125 MHz), δ 14.20 (NHCH$_2$*C*H$_3$), 48.37 (NH*C*H$_2$CH$_3$), 67.03 (*C*H$_2$ pyrrolidine), 68.40 (*C* attached to C_{60}), 68.54 (*C*H Cp ring), 68.68 (*C*H Cp ring), 68.90 (*C*H Cp ring), 69.67 (*C*H Cp ring), 70.58 (*C*H Cp ring), 70.99 (*C*H Cp ring), 74.45 (*C*H Cp ring), 74.61 (*C*H Cp ring), 75.69 (*C*H pyrrolidine), 77.85 (*C* attached to C_{60}), 79.74 (*Cq* Cp ring), 89.47 (*Cq* Cp ring), 135.60–156.23 (C_{60} and quaternary aromatic carbons), 193.51 (aldehyde). IR: 2921w, 2813w (ν_{C-H}), 1685s

($\nu_{C=O}$), 1463m, 1429m, 1371m, 1338m ($\nu_{C=C}$), 1267m, 1188m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1004 $[M]^-$.

Synthesis of Fc*t*BuAld

To a solution of *N*-chlorosuccinimide (60.0 mg, 0.493 mmol) and $AgNO_3$ (58.0 mg, 0.341 mmol) in acetonitrile : water 85 : 15 (35 mL) was added rapidly a solution of **FcS_2tBu** (54.8 mg, 0.046 mmol) in THF (50 mL) and the dark suspension stirred at r.t. for 4 h. To this was added a saturated solution of Na_2SO_3 (1 mL) and a saturated solution of $NaHCO_3$ (2 mL) and then brine (1 mL) at 1 min intervals. After the addition of CH_2Cl_2 (50 mL), the mixture was stirred at r.t. for 15 min. The resulting two layers were separated and the organic phase washed with water. The organic layers were combined and passed through a pad of cotton wool. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from toluene to ethyl acetate was used to yield **Fc*t*BuAld** as a brown solid (13.4 mg, 26%). NMR ($CDCl_3$): ^1H (500 MHz), δ 1.44 (s, 9H, C(CH_3)$_3$), 3.88 (d, ^2J = 13.1 Hz, 1H, NHCH_2Ph*t*Bu), 4.13 (d, ^2J = 9.6 Hz, 1H, CH_2 pyrrolidine), 4.39 (m, 1H, C*H* Cp ring), 4.42 (m, 1H, C*H* Cp ring), 4.71 (m, 1H, C*H* Cp ring), 4.77 (m, 2H, C*H* Cp ring), 4.81 (m, 2H, CH_2 pyrrolidine + C*H* Cp ring), 4.92 (m, 1H, C*H* Cp ring), 4.97 (m, 1H, C*H* Cp ring), 5.11 (s, 1H, C*H* pyrrolidine), 5.99 (d, ^2J = 13.1 Hz, 1H, NHCH_2Ph*t*Bu), 7.58 (d, ^3J = 8.4 Hz, 2H, aromatic C*H* Bn*t*Bu), 7.77 (d, ^3J = 8.4 Hz, 2H, aromatic C*H* Bn*t*Bu), 10.09 (s, 1H, aldehyde); ^{13}C (125 MHz), δ 31.49 (C(CH_3)$_3$), 34.66 (*C*(CH_3)$_3$), 57.98 (NHCH_2Ph*t*Bu), 67.61 (*C*H_2 pyrrolidine), 68.39 (*C* attached to C_{60}), 68.51 (*C*H Cp ring), 68.76 (*C*H Cp ring), 69.12 (*C*H Cp ring), 69.85 (*C*H Cp ring), 70.64 (*C*H Cp ring), 71.00 (*C*H Cp ring), 74.67 (*C*H Cp ring), 74.74 (*C*H Cp ring), 75.23 (*C*H pyrrolidine), 77.80 (*C* attached to C_{60}), 79.73 (*Cq* Cp ring), 89.07 (*Cq* Cp ring), 125.91 (aromatic *C*H Bn*t*Bu), 127.98 (aromatic *C*H Bn*t*Bu), 135.60–156.13 (C_{60} and quaternary aromatic carbons), 193.53 (aldehyde). IR: 2961w, 2924w, 2846w (ν_{C-H}), 1686s ($\nu_{C=O}$), 1513m, 1461m, 1429m, 1369m, 1337m ($\nu_{C=C}$), 1261m, 1183m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1122 $[M]^-$.

Synthesis of FcOhexAld

To a solution of *N*-chlorosuccinimide (41.0 mg, 0.307 mmol) and $AgNO_3$ (39.2 mg, 0.231 mmol) in acetonitrile : water 85 : 15 (35 mL) was added rapidly a solution of **FcS_2Ohex** (50.7 mg, 0.041 mmol) in THF (50 mL) and the dark suspension stirred at r.t. for 4 h. To this was added a saturated solution of Na_2SO_3 (1 mL), a saturated solution of $NaHCO_3$ (2 mL) and then brine (1 mL) with 1 min intervals between each addition. After the addition of CH_2Cl_2 (50 mL), the mixture was stirred at r.t. for 15 min. The resulting two layers were separated and the organic phase washed with water. The organic layers were combined and passed through a pad of cotton wool. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from toluene to ethyl acetate was used to yield **FcOhexAld** as a brown solid (13.3 mg, 28%). NMR ($CDCl_3$): ^1H (500 MHz), δ 0.93 (t, ^3J = 7.1 Hz, 3H, CH_3 alkyl chain), 1.39 (m, 4H, CH_2 alkyl chain), 1.52 (m, 2H, CH_2 alkyl chain), 1.85 (m, 2H, BnOCH_2CH_2), 3.82 (d, ^2J = 12.6 Hz, 1H, NHCH_2PhOhexyl), 4.06 (t, ^3J = 6.6 Hz, 2H, BnOCH_2), 4.11 (d, ^2J = 9.6 Hz, 1H, CH_2 pyrrolidine), 4.40 (m, 2H, C*H* Cp ring), 4.71 (m, 1H, C*H* Cp ring), 4.75 (m, 3H, CH_2 pyrrolidine + C*H* Cp ring), 4.82 (m, 1H, Cp ring), 4.92 (m, 1H, C*H* Cp ring), 4.97 (m, 1H, C*H* Cp ring), 5.09 (s, 1H, C*H* pyrrolidine), 5.93 (d, ^2J = 12.6 Hz, 1H, NHCH_2PhOhexyl), 7.09 (d, ^3J = 8.7 Hz, 2H, aromatic C*H* BnOhexyl), 7.73 (d, ^3J = 8.7 Hz, 2H, aromatic C*H* BnOhexyl), 10.09 (s, 1H, aldehyde); ^{13}C (125 MHz), δ 14.05 (*C*H_3 alkyl chain), 22.63 (*C*H_2 alkyl chain), 25.80 (*C*H_2 alkyl chain), 29.33 (*C*H_2 alkyl chain), 31.62 (*C*H_2 alkyl chain), 57.80 (NH*C*H_2PhOhexyl), 67.53 (*C*H_2 pyrrolidine), 68.15 (BnO*C*H_2), 68.29 (*C* attached to C_{60}), 68.48 (*C*H Cp ring), 68.81 (*C*H Cp ring), 69.12 (*C*H Cp ring), 69.84 (*C*H Cp ring), 70.66 (*C*H Cp ring), 71.01 (*C*H Cp ring), 74.63 (*C*H Cp ring), 74.69 (*C*H Cp ring), 75.17 (*C*H pyrrolidine), 77.86 (*C* attached to C_{60}), 79.75 (*Cq* Cp ring), 89.07 (*Cq* Cp ring), 114.92 (aromatic *C*H BnOhexyl), 129.54 (aromatic *C*H BnOhexyl), 135.59–158.76 (C_{60} and quaternary aromatic carbons), 193.54 (aldehyde) (Found: C, 88.67; H, 2.57; N, 1.18. $C_{86}H_{31}NOFe$ requires C, 88.59; H, 2.68; N, 1.20%). IR: 2961w, 2925w, 2853w (ν_{C-H}), 1684s ($\nu_{C=O}$), 1611w, 1510m, 1462m, 1429m, 1369m, 1336m ($\nu_{C=C}$), 1260m, 1170m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1166 $[M]^-$.

Synthesis of FcEt3 and FcEt4

To a solution of *N*-(ethyl)glycine (22.4 mg, 0.217 mmol) in dry toluene (30 mL) heated under reflux was added dropwise a solution of **FcEtAld** (35.2 mg, 0.035 mmol) in dried toluene (20 mL), and the brown mixture heated under reflux for 15 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcEt3** (7.3 mg, 20%) and **FcEt4** (2.6 mg, 7%) as brown solids.

For FcEt3. R_f (toluene) 0.54. NMR ($CDCl_3$): ^1H (500 MHz), δ 1.63 (t, ^3J = 7.0 Hz, 6H, NHCH$_2$CH_3), 2.63 (m, 4H, NHCH_2CH$_3$), 3.75 (d, ^2J = 9.3 Hz, 2H, CH_2 pyrrolidine), 3.82 (d, ^2J = 9.3 Hz, 2H, CH_2 pyrrolidine), 4.23 (m, 4H, NHCH_2CH$_3$), 4.38 (br s, 2H, C*H* Cp ring), 4.40 (br s, 2H, C*H* Cp ring), 4.68 (br s, 2H, C*H* Cp ring), 4.74 (br s, 2H, C*H* Cp ring), 5.13 (s, 2H, C*H* pyrrolidine) (Found: C, 89.75; H, 2.26; N, 2.66. $C_{78}H_{24}N_2Fe$ requires C, 89.66; H, 2.32; N, 2.68%). IR: 2965w, 2928w, 2837w (ν_{C-H}), 1513m, 1457m, 1425m, 1380m, 1328m ($\nu_{C=C}$), 1261m, 1184m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1044 $[M]^-$.

For FcEt4. R_f (toluene) 0.32. NMR ($CDCl_3$): ^1H (500 MHz), δ 1.63 (t, ^3J = 7.0 Hz, 6H, NHCH$_2$CH_3), 2.69 (m, 2H, NHCH_2CH$_3$), 3.84 (br s, 2H, CH_2 pyrrolidine), 4.12 (m, 4H, CH_2 pyrrolidine + C*H* Cp ring), 4.32 (m, 6H, C*H* Cp ring + NHCH_2CH$_3$), 4.52 (m, 2H, C*H* Cp ring), 4.99 (s, 2H, C*H* pyrrolidine). IR: 2958w, 2924w, 2851w (ν_{C-H}), 1508m, 1458m, 1400m, 1382m, 1336m ($\nu_{C=C}$), 1262m, 1197m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1044 $[M]^-$.

Synthesis of Fc*t*Bu1 and Fc*t*Bu2

To a solution of *N*-(4-(*tert*-butyl)benzyl)glycine **5** (58.7 mg, 0.265 mmol) in dry toluene (30 mL) heated under reflux was added dropwise a solution of **Fc*t*BuAld** (46.7 mg, 0.042 mmol) in dried toluene (20 mL), and the brown mixture heated under

reflux for 15 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **Fc*t*Bu1** (7.2 mg, 13%) and **Fc*t*Bu2** (3.5 mg, 5%) as brown solids.

For Fc*t*Bu1. R_f (toluene) 0.58. NMR ($CDCl_3$): ^{1}H (500 MHz), δ 1.30 (s, 18H, C(CH_3)$_3$), 3.36 (d, ^2J = 14.0 Hz, 2H, NHCH_2Ph*t*Bu), 3.69 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 3.77 (d, ^2J = 14.0 Hz, 2H, NHCH_2Ph*t*Bu), 3.90 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 4.27 (m, 2H, C*H* Cp ring), 4.41 (m, 2H, C*H* Cp ring), 4.73 (m, 2H, C*H* Cp ring), 4.79 (m, 2H, C*H* Cp ring), 5.13 (s, 2H, C*H* pyrrolidine), 7.31 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* Bn*t*Bu), 7.35 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* Bn*t*Bu); ^{13}C (125 MHz), δ 31.41 (C(*C*H$_3$)$_3$), 34.47 (*C*(CH$_3$)$_3$), 52.90 (NH*C*H$_2$Ph*t*Bu), 58.89 (*C*H$_2$ pyrrolidine), 66.07 (*C* attached to C$_{60}$), 67.89 (*C*H Cp ring), 70.75 (*C*H Cp ring), 71.08 (*C*H Cp ring), 71.57 (*C*H Cp ring), 71.66 (*C* attached to C$_{60}$), 72.49 (*C*H pyrrolidine), 83.17 (*Cq* Cp ring), 125.38 (aromatic *C*H Bn*t*Bu), 127.59 (aromatic *C*H Bn*t*Bu), 131.97–159.74 (C$_{60}$ and quaternary aromatic carbons). IR: 2962w, 2922w, 2851w (ν_{C-H}), 1513m, 1458m, 1413m, 1362m, 1327m ($\nu_{C=C}$), 1260m, 1190m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1283 [M]$^-$. UV-vis (Chloroform): λ/nm (ε/M^{-1} cm^{-1}) 445.0 (5.4×10^3), 634.2 (9.8×10^2), 702.8 (5.6×10^2).

For Fc*t*Bu2. R_f (toluene) 0.36. NMR ($CDCl_3$): ^{1}H (500 MHz), δ 1.30 (s, 18H, C(CH_3)$_3$), 3.69 (d, ^2J = 12.9 Hz, 2H, NHCH_2Ph*t*Bu), 3.75 (d, ^2J = 9.9 Hz, 2H, CH_2 pyrrolidine), 4.01 (d, ^2J = 9.9 Hz, 2H, CH_2 pyrrolidine), 4.13 (d, ^2J = 12.9 Hz, 2H, NHCH_2Ph*t*Bu), 4.18 (m, 2H, C*H* Cp ring), 4.27 (m, 2H, C*H* Cp ring), 4.28 (m, 2H, C*H* Cp ring), 4.30 (m, 2H, C*H* Cp ring), 5.14 (s, 2H, C*H* pyrrolidine), 7.36 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* Bn*t*Bu), 7.38 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* Bn*t*Bu); ^{13}C (125 MHz), δ 31.42 (C(*C*H$_3$)$_3$), 34.53 (*C*(CH$_3$)$_3$), 56.17 (NH*C*H$_2$Ph*t*Bu), 64.36 (*C*H$_2$ pyrrolidine), 67.97 (*C*H Cp ring), 68.45 (*C* attached to C$_{60}$), 71.02 (*C*H Cp ring), 71.34 (*C* attached to C$_{60}$), 71.41 (*C*H Cp ring), 73.78 (*C*H Cp ring), 76.39 (*C*H pyrrolidine), 85.40 (*Cq* Cp ring), 125.37 (aromatic *C*H Bn*t*Bu), 128.30 (aromatic *C*H Bn*t*Bu), 133.44–159.53 (C$_{60}$ and quaternary aromatic carbons). IR: 2961w, 2923w, 2851w (ν_{C-H}), 1514m, 1458m, 1414m, 1367m, 1342m ($\nu_{C=C}$), 1260m, 1190m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1283 [M]$^-$. UV-vis (chloroform): λ/nm (ε/M^{-1} cm^{-1}) 446.7 (3.9×10^3), 635.0 (7.7×10^2), 704.5 (4.3×10^2).

Synthesis of FcOhex3 and FcOhex4

To a solution of *N*-(4-(hexyloxy)benzyl)glycine (67.1 mg, 0.253 mmol) in dry toluene (30 mL) heated under reflux was added dropwise a solution of the **FcOhexAld** (44.0 mg, 0.038 mmol) in dried toluene (20 mL), and the brown mixture heated under reflux for 15 h under Ar. The solvent was removed *in vacuo* and the crude residue purified by silica gel column chromatography. A gradient elution from carbon disulfide to toluene was used to yield **FcOhex3** (8.5 mg, 16%) and **FcOhex4** (1 mg, 2%) as brown solids.

For FcOhex3. R_f (toluene) 0.57. NMR ($CDCl_3$): ^{1}H (500 MHz), δ 0.89 (t, ^3J = 7.1 Hz, 6H, CH_3 alkyl chain), 1.32 (m, 8H, CH_2 alkyl chain), 1.44 (m, 4H, CH_2 alkyl chain), 1.76 (m, 4H, BnOCH$_2$CH_2), 3.36 (d, ^2J = 13.7 Hz, 2H, NHCH_2PhOhexyl), 3.65 (d, ^2J = 9.3 Hz, 2H, CH_2 pyrrolidine), 3.68 (d, ^2J = 13.7 Hz, 2H, NHCH_2PhOhexyl), 3.92 (m, 6H, BnOCH_2 + CH_2 pyrrolidine), 4.23 (m, 2H, C*H* Cp ring), 4.40 (m, 2H, C*H* Cp ring), 4.71 (m, 2H, C*H* Cp ring), 4.78 (m, 2H, C*H* Cp ring), 5.07 (s, 2H, C*H* pyrrolidine), 6.83 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl), 7.33 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl); ^{13}C (125 MHz), δ 14.03 (*C*H$_3$ alkyl chain), 22.59 (*C*H$_2$ alkyl chain), 25.74 (*C*H$_2$ alkyl chain), 29.29 (*C*H$_2$ alkyl chain), 31.58 (*C*H$_2$ alkyl chain), 52.57 (NH*C*H$_2$PhOhexyl), 58.83 (*C*H$_2$ pyrrolidine), 65.89 (*C* attached to C$_{60}$), 67.86 (*C*H Cp ring), 67.92 (BnO*C*H$_2$), 70.68 (*C*H Cp ring), 71.04 (*C*H Cp ring), 71.58 (*C*H Cp ring), 71.60 (*C* attached to C$_{60}$), 72.11 (*C*H pyrrolidine), 83.09 (*Cq* Cp ring), 114.35 (aromatic *C*H BnOhexyl), 129.16 (aromatic *C*H BnOhexyl), 130.37–159.74 (C$_{60}$ and quaternary aromatic carbons) (Found: C, 87.75; H, 3.88; N, 1.90. $C_{100}H_{52}N_2O_2Fe$ requires C, 87.71; H, 3.83; N, 2.05%). IR: 2930w, 2851w (ν_{C-H}), 1610w, 1509m, 1458m, 1429m, 1367m, 1326m ($\nu_{C=C}$), 1241m, 1169m (δ_{C-H}) cm^{-1}. MALDI *m*/*z* 1369 [M]$^-$.

For FcOhex4. R_f (toluene) 0.37. NMR ($CDCl_3$): ^{1}H (500 MHz), δ 0.90 (t, ^3J = 7.1 Hz, 6H, CH_3 alkyl chain), 1.34 (m, 8H, CH_2 alkyl chain), 1.44 (m, 4H, CH_2 alkyl chain), 1.79 (m, 4H, BnOCH$_2$CH_2), 3.62 (d, ^2J = 12.8 Hz, 2H, NHCH_2PhOhexyl), 3.75 (d, ^2J = 9.5 Hz, 2H, CH_2 pyrrolidine), 3.97 (m, 6H, BnOCH_2 + CH_2 pyrrolidine), 4.12 (d, ^2J = 12.8 Hz, 2H, NHCH_2PhOhexyl), 4.17 (m, 2H, C*H* Cp ring), 4.27 (m, 6H, C*H* Cp ring), 5.14 (s, 2H, C*H* pyrrolidine), 6.90 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl), 7.33 (d, ^3J = 8.7 Hz, 4H, aromatic C*H* BnOhexyl); ^{13}C (125 MHz), δ 14.04 (*C*H$_3$ alkyl chain), 22.60 (*C*H$_2$ alkyl chain), 25.74 (*C*H$_2$ alkyl chain), 29.28 (*C*H$_2$ alkyl chain), 31.60 (*C*H$_2$ alkyl chain), 56.07 (NH*C*H$_2$PhOhexyl), 64.42 (*C*H$_2$ pyrrolidine), 68.05 (*C*H Cp ring), 68.50 (*C* attached to C$_{60}$), 70.97 (*C*H Cp ring), 71.34 (*C* attached to C$_{60}$), 71.44 (*C*H Cp ring), 73.77 (*C*H Cp ring), 76.22 (*C*H pyrrolidine), 85.45 (*Cq* Cp ring), 114.41 (aromatic *C*H BnOhexyl), 129.89 (aromatic *C*H BnOhexyl), 133.33–159.51 (C$_{60}$ and quaternary aromatic carbons). MALDI *m*/*z* 1369 [M]$^-$.

Acknowledgements

Maria Lebedeva recorded the CV of C$_{60}$ (SI file). We thank the EPSRC and the EU (Marie Curie Fellowship to DM) for funding. MS and ANK gratefully acknowledge receipt of an ERC Advanced Grant and an ERC Early Career Starter Grant, respectively.

References

1 *The Photosynthetic Reaction Center*, ed. J. Deisenhofer, J. R. Norris, Academic Press, San Diego, 1993.
2 D. Gonzalez-Rodriguez, T. Torres, D. M. Guldi, J. Riviera, M. Angeles Herranz and L. Echegoyen, *J. Am. Chem. Soc.*, 2004, **126**, 6301.
3 D. M. Guldi, M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1997, **119**, 974.

4 H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537.
5 H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, 2445.
6 D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22.
7 S. Leach, M. Vervloet, A. Desprès, E. Bréheret, J. P. Hare, T. J. Dennis, H. W. Kroto, R. Taylor and D. R. M. Walton, *Chem. Phys.*, 1992, **160**, 451.
8 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 40.
9 R. Fong, D. I. Schuster and S. R. Wilson, *Org. Lett.*, 1999, **1**, 729.
10 H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki and Y. Sakata, *J. Phys. Chem. B*, 2000, **104**, 2099.
11 H. Imahori, H. Yamada, S. Ozawa, Y. Sakata and K. Ushida, *Chem. Commun.*, 1999, 1165.
12 H. Imahori, N. Norteda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 100.
13 C. Luo, D. M. Guldi, H. Imahori, K. Tamaki and Y. Sakata, *J. Am. Chem. Soc.*, 2000, **122**, 6535.
14 A. S. D. Sandanayaka, K.-I. Ikeshita, Y. Araki, N. Kihara, Y. Furusho, T. Takata and O. Ito, *J. Mater. Chem.*, 2005, **15**, 2276.
15 F. D'Souza, S. Gadde, D. M. Shafiqul Islam, C. A. Wijesinghe, A. L. Schumacher, M. E. Zandler, Y. Araki and O. Ito, *J. Phys. Chem. A*, 2007, **111**, 8552.
16 T. Torres, A. Gouloumis, D. Sanchez-Garcia, J. Jayawickramarajah, W. Seitz, D. M. Guldi and J. L. Sessler, *Chem. Commun.*, 2007, 292.
17 D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. A. Herranz and L. Echegoyen, *J. Am. Chem. Soc.*, 2004, **126**, 6301.
18 J. Llaclay, J. Vecíana, J. Vídal-Gancedo, J. L. Bourdelande, R. González-Moreno and C. Rovira, *J. Org. Chem.*, 1998, **63**, 5201.
19 N. Martín, L. Sánchez, M. A. Herranz and D. M. Guldi, *J. Phys. Chem. A*, 2000, **104**, 4648.
20 M. C. Diaz, M. A. Herranz, B. M. Illescas, N. Martín, N. Godbert, M. R. Bryce, C. Luo, A. Swartz, G. Anderson and D. M. Guldi, *J. Org. Chem.*, 2003, **68**, 7711.
21 F. Giacalone, J. L. Segura, N. Martin, J. Ramey and D. M. Guldi, *Chem.–Eur. J.*, 2005, **11**, 4819.
22 G. Kodis, P. A. Liddell, A. L. Moore, T. A. Moore and D. Gust, *J. Phys. Org. Chem.*, 2004, **17**, 724.
23 M. E. Zandler, P. M. Smith, M. Fujitsuka, O. Ito and F. D'Souza, *J. Org. Chem.*, 2002, **67**, 9122.
24 F. D'Souza, M. E. Zandler, P. M. Smith, G. R. Deviprasad, K. Arkady, M. Fujitsuka and O. Ito, *J. Phys. Chem. A*, 2002, **106**, 649.
25 D. M. Guldi, M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1997, **119**, 974.
26 M. Maggini and M. Prato, *Acc. Chem. Res.*, 1998, **31**, 519.
27 F. Langa, P. de la Cruz, E. Espildora, A. Gonzalez-Cortes, A. de la Hoz and V. Lopez-Arza, *J. Org. Chem.*, 2000, **65**, 8675.
28 H. Imahori, H. Tamaki, H. Yamada, K. Yamada, Y. Sakata, Y. Nishimura, I. Yamazaki, M. Fujitsuka and O. Ito, *Carbon*, 2000, **38**, 1599.
29 T. Kuwana, D. E. Bublitz and G. Hoh, *J. Am. Chem. Soc.*, 1960, **82**, 5811.
30 R. J. Gale and R. Job, *Inorg. Chem.*, 1981, **20**, 42.
31 S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1847.
32 C. Cauletti, J. C. Green, M. R. Kelly, J. Robbins and J. C. Smart, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **19**, 327.
33 S. Barlow, L. M. Henling, M. W. Day, W. P. Schaefer, J. C. Green, T. Hascall and S. R. Marder, *J. Am. Chem. Soc.*, 2002, **124**, 6285.
34 S. Barlow and S. R. Marder, *Chem. Commun.*, 2000, 1555.
35 S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715.
36 J. J. Oviedo, P. de la Cruz, J. Garín, J. Orduna and F. Langa, *Tetrahedron Lett.*, 2005, **46**, 4781.
37 J. J. Oviedo, M. E. El-Khouly, P. de la Cruz, L. Perez, J. Garín, J. Orduna, Y. Araki, F. Langa and O. Ito, *New J. Chem.*, 2006, **30**, 93.
38 V. Mamane and O. Riani, *Tetrahedron*, 2001, **57**, 2555; M. A. Lebedeva, T. W. Chamberlain, M. Schröder and A. N. Khlobystov, *Tetrahedron*, 2012, **68**, 4976.
39 B. J. Farrington, M. Jevric, G. A. Rance, A. Ardavan, A. N. Khlobystov, G. A. D. Briggs and K. Porfyrakis, *Angew. Chem., Int. Ed.*, 2012, **51**, 1.
40 Z. Zhou, D. I. Schuster and S. R. Wilson, *J. Org. Chem.*, 2006, **71**, 1545.
41 S. Campidelli, E. Vázquez, D. Milic, M. Prato, J. Barberá, D. M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci and R. Deschenaux, *J. Mater. Chem.*, 2004, **14**, 1266.
42 B. Basu, S. K. Chattopadhyay, A. Ritzén and T. Frejd, *Tetrahedron: Asymmetry*, 1997, **8**, 1841.
43 K. Kordatos, S. Bosi, T. Da Ros, A. Zambon, V. Lucchini and M. Prato, *J. Org. Chem.*, 2001, **66**, 2802.
44 Q. Lu, D. I. Schuster and S. R. Wilson, *J. Org. Chem.*, 1996, **61**, 4764.
45 A. Hirsch, I. Lamparth and H. R. Karfunkel, *Angew. Chem., Int. Ed.*, 1994, **33**, 437.
46 Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.
47 C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075.
48 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.
49 N. Armaroli, G. Accorsi, F. Y. Song, A. Palkar, L. Echegoyen, D. Bonifazi and F. Diederich, *ChemPhysChem*, 2005, **6**, 732.
50 P. L. Boulas, M. Gomez-Kaifer and L. Echegoyen, *Angew. Chem., Int. Ed.*, 1998, **37**, 216.
51 A. Salzer, A. Bauer, S. Geyser and F. Podewils, *Inorg. Synth.*, 2004, **34**, 59.
52 R. F. G. Fröhlich, A. A. Zabelinskaja-Mackova, M. H. Fechter and H. Griengl, *Tetrahedron: Asymmetry*, 2003, **14**, 355.
53 U. T. Mueller-Westerhoff, Z. Yang and G. Ingram, *J. Organomet. Chem.*, 1993, **463**, 163.
54 G. G. A. Balavoine, G. Doisneau and T. Fillebeen-Khan, *J. Organomet. Chem.*, 1991, **412**, 381.