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Functionalised polyferrocene complexes: synthesis and mixed-valency properties

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We have synthesised three types of hexamers bearing 6 or 12 electro-active groups by a cyclotrimerisation reaction of symmetric alkynes. Two types of electro-active groups were added to the ferrocene, being introduced either before (case of Rubipy) or after (case of BDT) cyclotrimerisation. While the characterisation of compounds with the BDT functionalisation can be carried out by NMR due to the complete symmetry of these molecules, complexes bearing the Rubipy fragment are obtained as mixtures of diastereoisomers and were characterised using electrospray or FAB mass spectrometric techniques. Alkynes and hexamers functionalised by the BDT group (**1** and **2**) gave interesting spectrochemical properties. Indeed, in the case of molecules bearing a double bond between the ferrocene and the phenyl core (**1b** and **2b**), two mono-electronic oxidation waves are observed in the CVs, corresponding to the successive oxidation of two ferrocenes. In the case of **2b** an intervalence band is observed in NIR region.

Introduction

Electron transfer (ET) reactions[1] are one of the most fundamental processes in chemistry[2] and biology.[3] Thus, numerous investigations have been devoted to the study of ET processes in real biological systems,[4] in biomimetic model compounds,[5] and in structurally simple and completely artificial low molecular weight systems.[6] The preparation of the first mixed-valence (MV) complex by Creutz and Taube in 1969[7] opened a new area for the study of ET. In MV complexes, ET may be studied under controlled intramolecular conditions: across a fixed distance, between two fragments with known properties and through a ligand whose conformation and electronic characteristics are well-defined. The aims range from the desire to understand ET processes in nature to the design of molecular wires for electronic communication.[8]

Owing to its high stability, ease of functionalisation, and well-defined electrochemistry, ferrocene has been widely used as redox-active centres that are linked together with a wide variety of structural units such as saturated and unsaturated carbon bridges,[9] delocalised fused rings,[9] and polymeric and dendritic backbones.[10,11] To the best of our knowledge, multiferrocenyl systems in which each ferrocene is attached to another electro-active group (organic or inorganic) are not known. Here we present the synthesis and electrochemical study of hexaferrocenyl molecules having each ferrocene linked to an organic group (benzodithiolene) or an inorganic group (Ru bipyridines) for the generation of MV complexes.

Results and discussion

Synthesis

In a previous communication we described the synthesis and preliminary electrochemical behaviour of four enantiopure polyferrocene complexes **1**–**2**[12] (Scheme 1). In these complexes each ferrocene is linked to an organic electro-active benzodithiolene (BDT) group. A full account concerning the synthesis of these compounds as well as a more detailed electrochemical and spectroscopic study is provided here. We also wish to describe the synthesis and electrochemical behaviour of the new polyferrocene complexes **3** and **4** (Scheme 1) in which each ferrocene is attached to a ruthenium bipyridine (Rubipy) moiety.

Two types of complexes have thus been synthesised, which differ by the presence or not of a double bond between the ferrocene and the phenyl core (Scheme 1). This structural difference led us to consider two different pathways to introduce the chiral ferrocene moiety. As depicted in Scheme 2, the monomer **7a** is obtained with 72% yield using a palladium-catalysed cross-coupling reaction between a chiral orthometallated ferrocenyl zinc intermediate and bis(*p*-bromophenyl)-acetylene, followed by deprotection of the acetal groups.[13] The vinyl analogue monomer **7b**[14] was obtained in 64% yield by Siegrist condensation of two equivalents of the imine **6**[14] with bis(*p*-tolyl)acetylene and subsequent deprotection of the acetal groups. The [2 + 2 + 2] cyclotrimerisations of alkynes **7a** and **7b** were carried out in refluxing dioxane in the presence of a catalytic amount (10 mol %) of dicobalt octacarbonyl. Clean conversion was observed in both cases and the corresponding enantiopure cyclotrimers **8a** and **8b** were isolated as stable orange crystalline solids in 85% yield (Scheme 3).

The introduction of BDT groups on each ferrocene in monomers **7a**, **7b** and cyclotrimers **8a**, **8b** was carried out using a standard Wittig–Horner condensation. The two- and six-fold condensation of phosphonate **9**[15] on the bisaldehydes **7a**, **7b** and hexaaldehydes **8a**, **8b** were conducted using *t*-BuOK as a base in THF and gave the new enantiopure derivatives **1a**, **1b** and **2a**, **2b**, bearing, respectively, 4 and 12 electro-active units, in moderate to good yields (Scheme 3).

Ruthenium containing cyclotrimers **4a**, **4b** were synthesised in three steps from monomers **7a**, **7b**. Bisaldehydes **7a**, **7b** were condensed with phosphine oxide **10**[16] in good yields to give compounds **11a**, **11b** bearing bipyridine group on each ferrocene. Complexation of the ruthenium moiety is performed by refluxing compounds **11a**, **11b** in ethanol. Complexes **12a**–**12d** were obtained in moderate yields after precipitation with ammonium hexafluorophosphate and purification by

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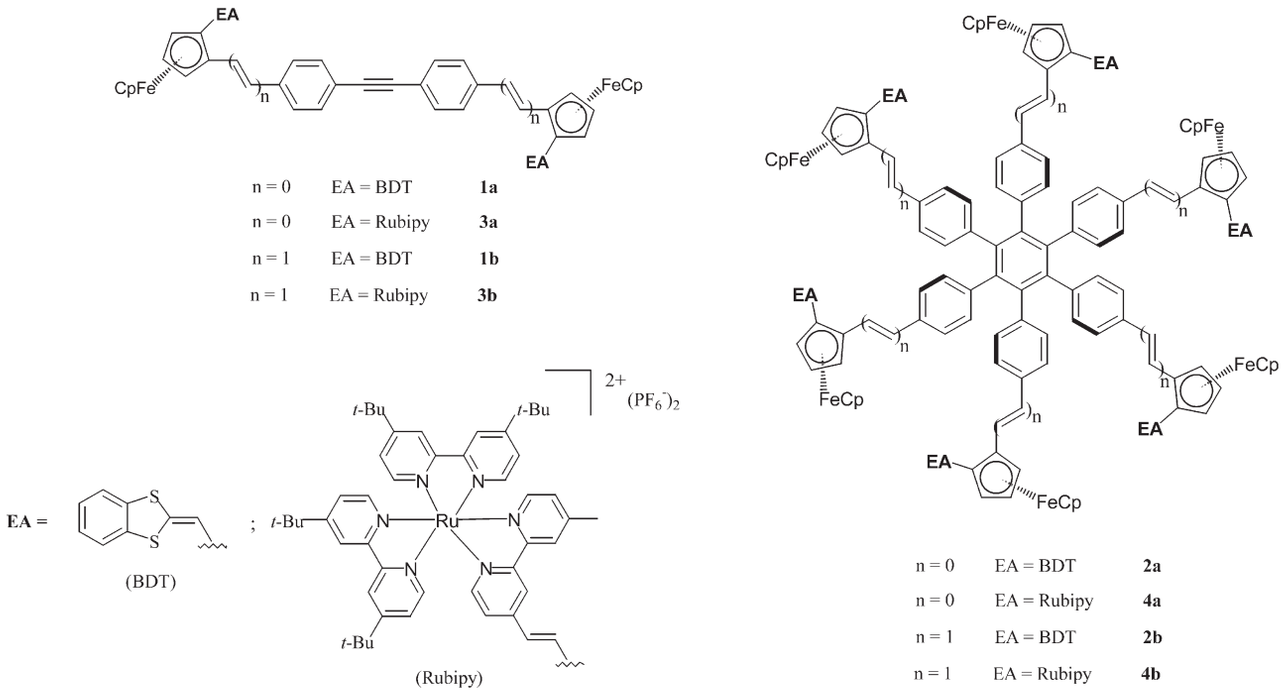


Scheme 1

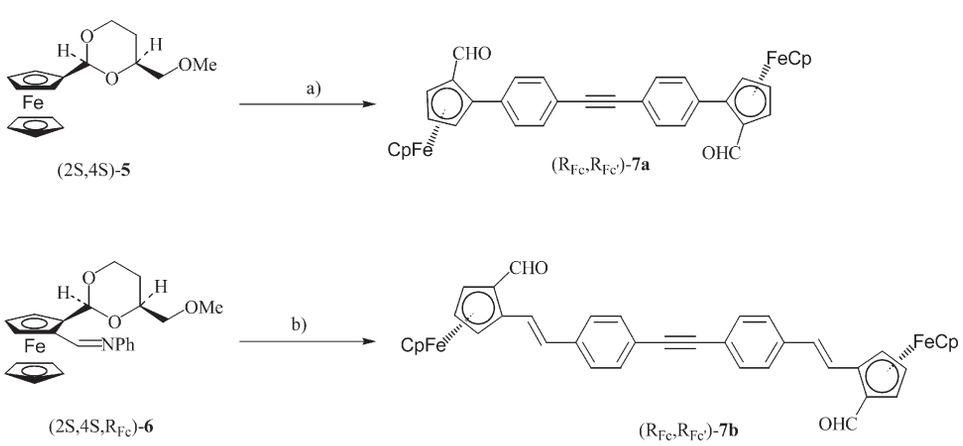
chromatography on silica gel (Scheme 4). The ^{1}H NMR analysis displayed a complex spectra, which was attributed to the presence of a diastereoisomeric mixture due to the introduction of two new chiral ruthenium centres. During our early experiments, we tried to cyclotrimerise complexes **12c**, **12d** bearing unsubstituted bipyridine ligands. However, the corresponding complexes are completely insoluble in dioxane, even at refluxing conditions. No conversion was also obtained by using acetonitrile as a cosolvent of dioxane as the presence of acetonitrile seems to accelerate the decomposition of the catalyst. Introduction of several *tert*-butyl groups on bipyridines increases the solubility of these complexes in non-coordinating solvents such as chlorinated solvents.

Finally, [2 + 2 + 2] cyclotrimerisations of complexes **12a**, **12b** were successfully performed by reacting the monomers with a catalytic amount (10 mol %) of dicobalt octacarbonyl in a refluxing mixture of 1,2-dichloroethane–dioxane (Scheme 5). After purification by chromatography on silica gel, cyclotrimers **4a** and **4b** were isolated in 70% and 53% yields, respectively. The presence of a mixture of diastereomers is revealed in the ^{1}H NMR spectra by broad peaks.

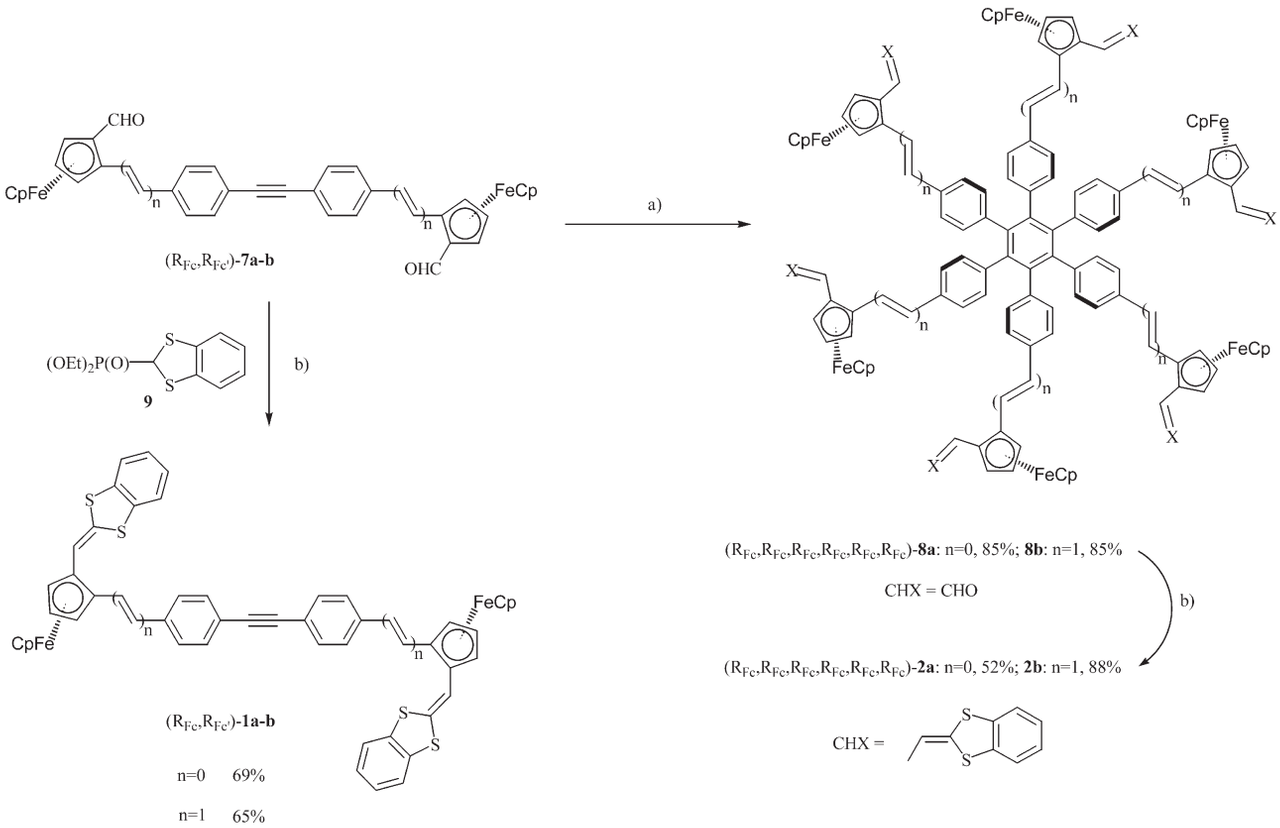
Mass spectrometry of ruthenium complexes

As mentioned above, characterisation of complexes **12** and **13** by NMR spectroscopy was made difficult due to the presence of a diastereoisomeric mixture. Obtaining an unequivocal structure analysis of these complexes required a mass spectroscopic analysis. Complexes **12** were easily analysed by electrospray ionisation (ESI) mass spectroscopy, which showed molecular ions M^{4+} and M^{3+}. In the case of complex **12c** we also observed the molecular ions M^{2+} and M^{+}.

Electrospray MS spectra of complexes **12a** and **12b** are represented in Fig. 1 For **12a**, the molecular ion M^{4+} is observed at $m/z = 553.2$ (calcd $m/z = 553.1$) and M^{3+} ($M^{4+} + PF_6^-$) at $m/z = 785.6$ (calcd $m/z = 785.8$). Electrospray MS spectra of **12b** shows the molecular ion M^{4+} at $m/z = 565.5$ (calcd $m/z = 565.6$) and M^{3+} at $m/z = 802.3$ (calcd $m/z = 802.5$). Hexamers **4a** and **4b** were analysed by



Scheme 2 (a) (*i*) *t*-BuLi, OEt_2; (*ii*) $ZnCl_2$, THF; (*iii*) bis(*p*-bromophenyl)acetylene, 5% $PdCl_2(PPh_3)_2$; (*iv*) PTSA, CH_2Cl_2, H_2O (72%). (b) (*i*) bis(*p*-tolyl)acetylene, *t*-BuOK, DMF; (*ii*) PTSA, CH_2Cl_2, H_2O (64%).

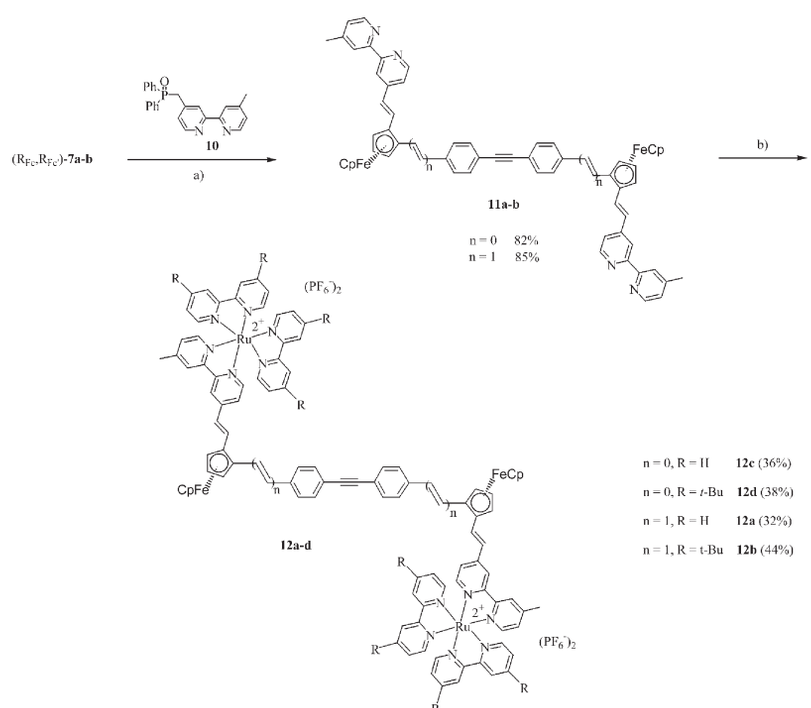


Scheme 3 (a) 10% $Co_2(CO)_8$, dioxane, reflux. (b) **9**, *t*-BuOK, THF.

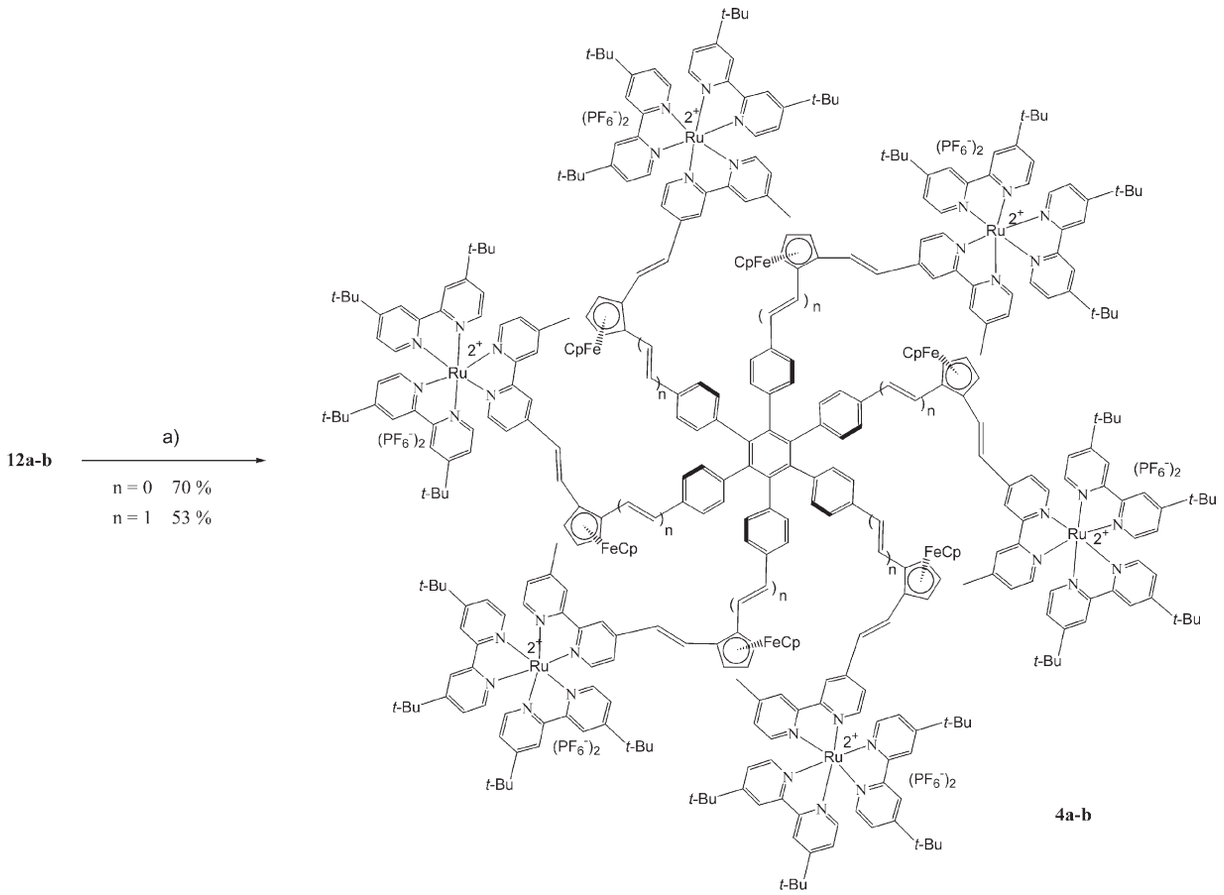
FAB mass spectroscopy. In each case, molecular ions M^{4+}, M^{5+}, M^{6+} and M^{7+} were observed, as well as M^{3+} for **4a**.

Mixed-valency properties

Results of cyclic voltammetry of compounds **7**, **8** and BDT fonctionalised molecules **1**, **2** are presented in Table 1. For comparison, ferrocene (Fc), ferrocenecarboxaldehyde (FcCHO) and compounds **13**, **14** and **15** drawn in Scheme 6 are also presented. For compounds **7a**, **7b** and **8a**, **8b** cyclic voltammograms (CV) show a quasi-reversible one-electron oxidation in which all the ferrocenes appear to be equivalent. For these 4 compounds, the preparative electrolysis in acetonitrile–dichloromethane mixtures gave very insoluble and



Scheme 4 (a) **10**, NaH, THF, reflux. (b) (*i*) *cis*-$RuCl_2(bipy)_2$ or *cis*-$RuCl_2(bipy^*)_2$, EtOH, reflux; (*ii*) NH_4PF_6.



Scheme 5 (a) 10% $Co_2(CO)_8$, 1,2-dichloroethane–dioxane (4:1), 100 °C.

unstable products, therefore the study of the oxidised forms by absorption spectroscopy was impossible and our interest turned to functionalised ferrocene molecules.

By comparison of compounds **13** and **14**, we can attribute the first quasi-reversible and mono-electronic wave to the oxidation of the ferrocenyl fragment. For **13** we observe a second wave, irreversible and attributed to the BDT group, a result in concordance with the work of Togni *et al.*[17] who found that compound **15** (Schema 6) shows an irreversible oxidation at higher potentials (+0.93 *vs.* SCE). The presence of the strong donor BDT group on the ferrocene fragment in compound **13** causes a strong displacement of the first wave to lower potential (nearly 800 mV) compared to **14**. This result, combined with the fact that the BDT group is also oxidised at lower potential, proves that there is a strong interaction between the ferrocene and BDT groups.

For compounds **1a** and **2a** (molecules without double bonds), the first wave is reversible and mono-electronic while the second oxidation leads to a strong adsorption onto the electrode [Fig. 2(a)]. Alkyne **1b** shows two well-resolved, quasi-reversible and mono-electronic oxidation waves [Fig. 2(b)]. Complex **2b** present two closed oxidation waves, which correspond to multi-electronic transfers for which the number of transferred electrons has not been determined. In the cases of **1b** and **2b** the second oxidation can be unambiguously attributed to a second ferrocene. Indeed, this wave cannot be attributed to oxidation of BDT, which is irreversible and at higher potential. Analysis by UV/Vis/NIR of the solution

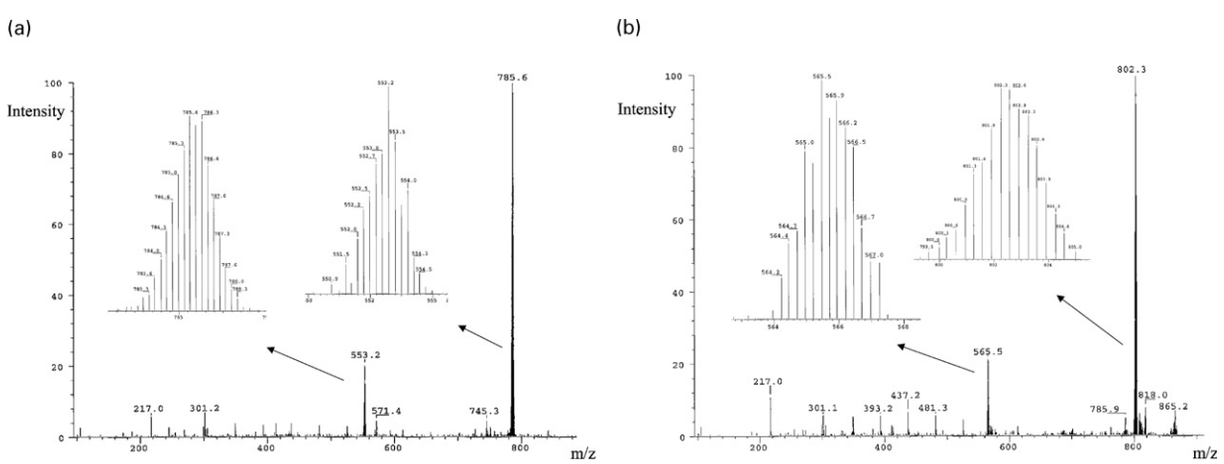


Fig. 1 Electrospray MS spectra of (a) **12a** and (b) **12b**.

Table 1 Formal electrode potentials (in V *vs.* SCE) for the ferrocenyl centred oxidation of ferrocene (Fc), ferrocenecarboxaldehyde (FcCHO) and compounds **7**, **8**, **13**, **14**, **1** and **2**[a]

Compound	$E_{1/2}$ (1)/V	$E_{1/2}$ (2)/V	ΔE/V
Fc	0.5	–	–
FcCHO	0.83	–	–
7a	0.85	–	–
7b	0.8	–	–
8a	0.84	–	–
8b	0.67	–	–
13	−0.4	0.34[b]	–
14	0.42	–	–
1a	−0.39	0.16[c]	–
1b	−0.42	0.18	0.6
2a	−0.43	0.03[c]	–
2b	0.38	0.5	0.12

[a] Experimental conditions: CH_2Cl_2–CH_3CN 2:1 (v:v), TBAP (0.1 M); concentration in electro-active compound: 5×10^{-3} M; 2 mm^2 glassy carbon working electrode; SCE reference; 100 mV s^{-1} sweep rate, 20 °C. [b] Irreversible $E_{p,ox}$. [c] Adsorption $E_{p,ox}$.

obtained by preparative oxidation of **2b** carried out at +0.68 V *vs.* SCE showed that the characteristic band at 450 nm of the ferrocene disappears with the appearance of two new bands: one at 550 nm that is characteristic of the ferricinium ion and another band in the NIR at 1393 nm (Fig. 3). This second band represents the intervalence band that corresponds to electron transfer between two electro-active centres of the VM complex obtained by oxidation of complex **2b**.

In Table 2 are presented the results of cyclic voltammetry obtained for compounds **4**, **11**, **12** and the monomeric analogues **16**, **17**[18] (Scheme 7). These compounds show three regions of electro-activity. (1) Between 0.4 and 0.5 V *vs.* SCE, we observe the oxidation of the ferrocene, which is in all cases reversible or quasi-reversible. (2) Between 1 and 1.3 V *vs.* SCE the irreversible oxidation (irrev) of ruthenium(II) occurs. (3) Between −1.4 and −2.2 V *vs.* SCE, the CVs show the reduction in three steps of the bipyridines (bipy) coordinated to the ruthenium. In the mononuclear compounds **17a** and **17b** these three reduction waves are completely reversible. Increasing the number of electro-active centres causes almost no effect on the oxidation potentials of the ferrocene and the ruthenium. However, the reduction waves of the bipy ligands become irreversible. These first electrochemical results indicate that there is no electronic coupling between ferrocenes.

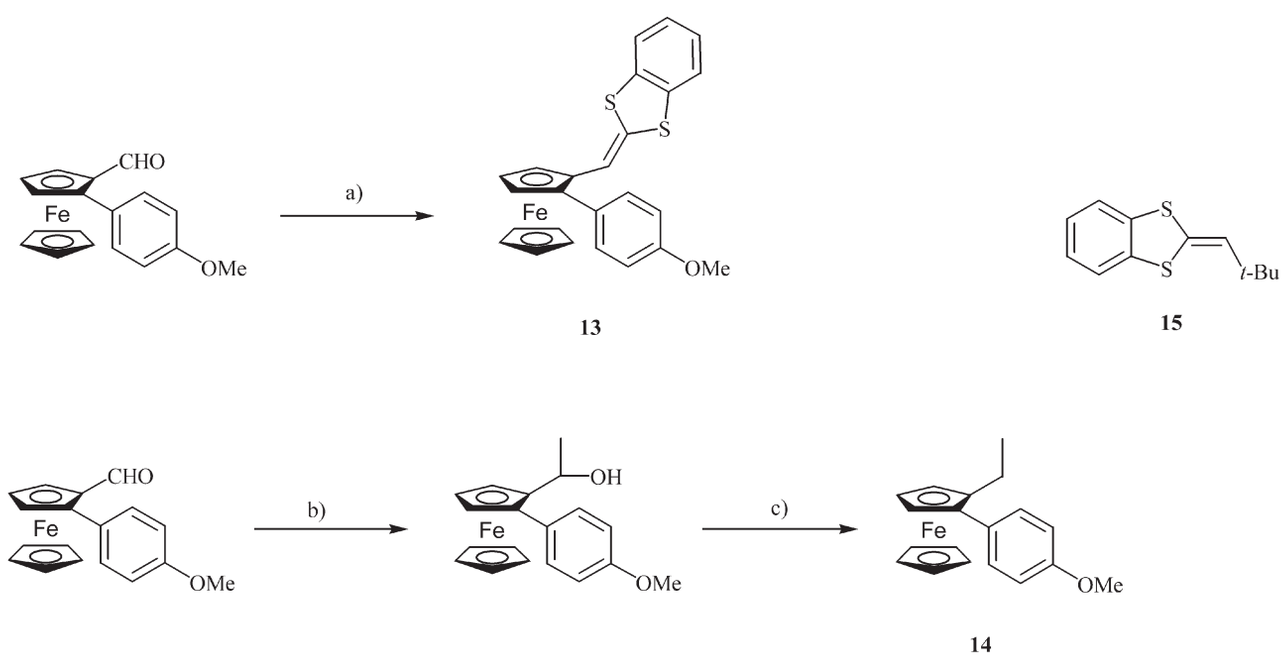
Conclusions

We have synthesised three types of hexamers bearing 6 or 12 electro-active groups. Unfunctionalised hexamers **8a**, **8b** were obtained in three steps from the chiral acetal **5**. After a palladium-catalysed cross-coupling reaction or a Siegrist condensation, the resulting alkynes were hydrolysed and cyclotrimerised to give hexamers **8a**, **8b**. The second electro-active group can be introduced either before the cyclotrimerisation reaction, as in the case of the Rubipy fragment, or afterwards, as for the BDT group. While the characterisation of compounds **1** and **2** can be done by NMR due to the complete symmetry of the molecules, complexes **3** and **4** bearing the Rubipy fragment were obtained as mixtures of diastereoisomers and characterised using ESI-MS or FAB-MS techniques. All hexameric compounds and the corresponding alkynes were studied by cyclic voltammetry. The most interesting results are obtained in the case of the alkynes and hexamers functionalised by the BDT group (molecules **1** and **2**). Indeed, in the case of molecules with a double bond between the ferrocene and the phenyl core (**1b** and **2b**), we observe in the CVs two mono-electronic oxidation waves (not well-resolved for **2b**) corresponding to the successive oxidation of two ferrocenes (for **2b**, the number of electrons involved in each oxidation has not been determined). At potentials between these two waves, MV complexes exist and in the case of **2b**, we observe an intervalence band in the NIR that is characteristic of an electron transfer between two electro-active centres. Efforts are now under way to try to isolate MV complexes for a complete physical study.

Experimental

General methods

Melting points were determined on a Reichert apparatus. IR spectra were recorded using a Perkin–Elmer FTIR 1600 spectrometer and are reported in wave numbers (cm^{-1}). UV-VIS spectra were recorded on a Kontron spectrometer. Optical



Scheme 6 (a) **9**, *t*-BuOK, THF (100%). (b) MeMgBr, OEt_2. (c) $LiAlH_4$–$AlCl_3$, OEt_2 (92% over two steps).

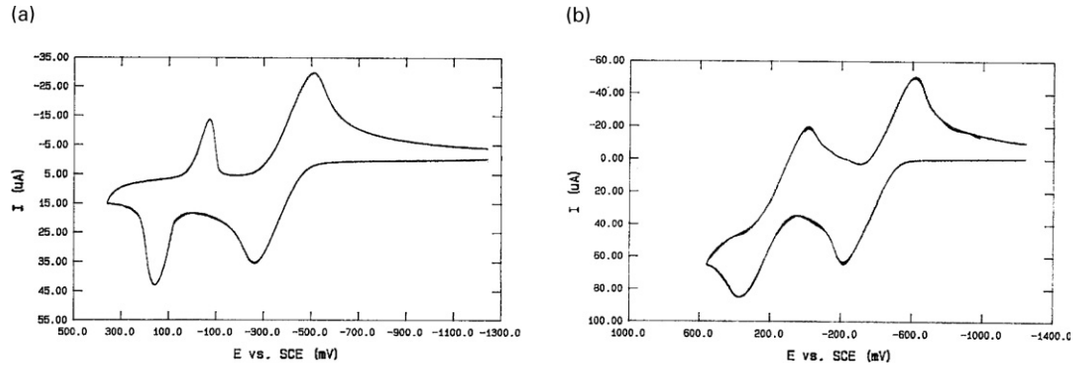


Fig. 2 CV curves of alkynes **1a** (left) and **1b** (right). In the case **1a**, the adsorption at the electrode is characterised by a sharp peak. The scan rate is 100 mV s^{-1}.

rotations were measured on a Perkin–Elmer 241 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on Brucker AC 200 (200 and 50 MHz) and AC 250 (250 and 63 MHz) machines. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. As the internal reference, the solvent signal [^{1}H: $\delta(CDCl_3) = 7.27$; ^{13}C: $\delta(CDCl_3) = 77.0$] was used. EI mass spectra (70 eV) were measured on a Riberg Mag R10-10. HR-MS and electrospray ionisation (ESI) mass spectra were determined using a Finnigan MAT-95-S apparatus. FAB-MS spectra were determined using a Finnigan MAT TSQ–70 equipped with a Xenon ION TECH 8 kV canon beam.

THF and Et_2O were distilled from Na/benzophenone, DMF and acetonitrile from CaH_2, and CH_2Cl_2 from P_2O_5. All air- or moisture-sensitive reactions were carried out in dry glassware under Ar. Flash column chromatography was performed employing 60 Å C.C. 35–70 μm silica gel.

Syntheses

(R_{Fc},$R_{Fc'}$)-1,2-Bis[4′-(α-formylferrocenyl)-1′-phenyl]acetylene, 7a. A solution of acetal **5**[19] (10 mmol, 3.16 g) in dry degassed diethyl ether (40 ml) was treated with a pentane solution of *t*-butyl lithium (1.6 M, 20 mmol, 14 ml) at −78 °C for 10 min. The reaction was warmed to RT and stirred for 1 h. To the resulting orange suspension was added at −78 °C a freshly prepared solution of anhydrous zinc chloride (0.5 M in THF, 11 mmol, 22 ml). The solution was warmed to RT. and stirred for 1 h. To the mixture was added $PdCl_2(PPh_3)_2$ (0.5 mmol, 315 mg, 5%), followed by bis(4-bromophenyl)acetylene (4.5 mmol, 1.512 g). After being stirred at RT overnight the mixture was treated with a saturated solution of ammonium chloride and extracted with Et_2O. The organic phase was dried over $MgSO_4$, the solvent evaporated, and the residue was purified by column chromatography on silica gel (Et_2O–cyclohexane 2:1). The diacetal was isolated as a light orange solid (2.6 g, 3.22 mmol, 72% yield). Mp 88 °C, $[\alpha]_D^{23}$ −471 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.47 (2H, m, CH_2), 1.81 (2H, m, CH_2), 3.36 (6H, s, CH_3), 3.46 (4H, m, CH_2–O), 3.96 (2H, m, CH_2–O), 4.09 (10H, s, Cp), 4.29 (2H, m, $Cp_{subst.}$), 4.56 (2H, m, $Cp_{subst.}$), 4.58 (2H, m, $Cp_{subst.}$), 5.46 (2H, s, O–CH–O), 7.46 (4H, d, $J = 8.1$ Hz, aromatics), 7.65 (4H, d, 8.1 Hz, aromatics); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 26.9, 27.8, 59.3, 67.0, 67.75, 67.9, 70.55, 71.05, 75.45, 76.1, 83.0, 85.95, 89.75, 99.9, 120.9, 129.0, 131.1, 139.0; HR-MS *m*/*z* calcd for $C_{46}H_{46}Fe_2O_6$: 806.1993; found: 806.2003.

The diacetal (3.22 mmol, 2.6 g) was dissolved in CH_2Cl_2 (70 ml). Water (30 ml) and *p*-toluenesulfonic acid (32.2 mmol, 6.2 g) were added and the mixture was stirred vigorously for 2 h at RT. A saturated solution of $NaHCO_3$ was added and the organic phase was separated, dried over $MgSO_4$ and concentrated. After filtration on silica gel (Et_2O–CH_2Cl_2 1:1) and recrystallisation from Et_2O, the product **7a** was isolated as an orange solid (1.85 g, 3.2 mmol, 95% yield). Mp 108 °C, $[\alpha]_D^{23}$ +341 (*c* 0.088, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.24 (10H, s, Cp), 4.73 (2H, m, $Cp_{subst.}$), 4.86 (2H, m, $Cp_{subst.}$),

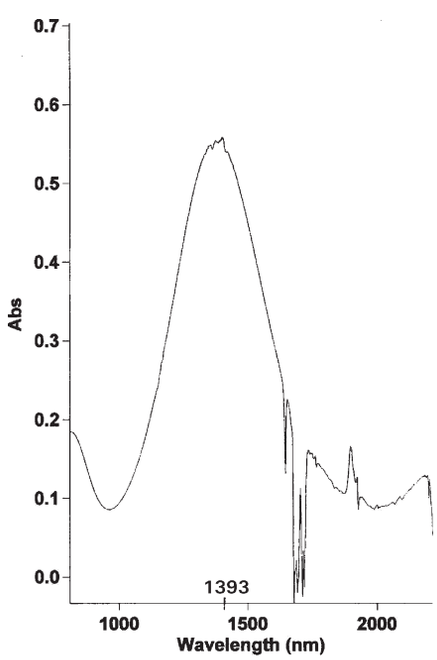
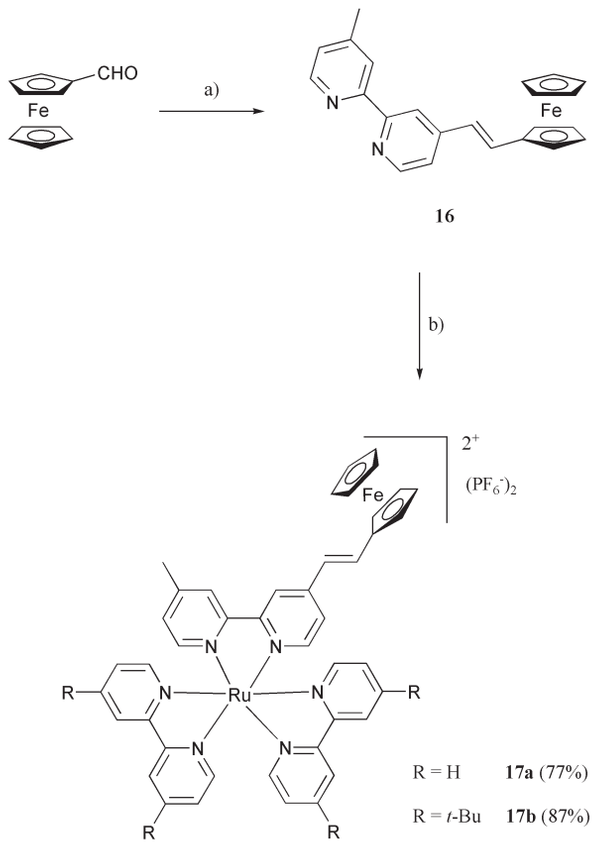


Fig. 3 Intervalence band observed after preparative oxidation of complex **2b**.

Table 2 Half-wave potentials ($E_{1/2}$), oxidation potentials ($E_{p,ox}$) and reduction potentials ($E_{p,red}$) of compounds **4**, **11**, **12**, **16** and **17**[a]

Compound	$E_{1/2}$ ($Fc/Fc^{+\bullet}$)/V	$E_{p,ox}$ (Ru^{II}/Ru^{III})/V	$E_{1/2}$ or $E_{p,red}$ (bipy)/V
16	0.50	–	–
17a	0.41	1.21	−1.45 to −1.87[b]
17b	0.41	1.18	−1.49 to −1.98[b]
11a	0.56	–	–
11b	0.54	–	–
12a	0.43	1.20, 1.60	−1.38 to −2[c]
12b	0.44	1.16	−1.46 to −2[c]
12c	0.48	1.23	−1.40 to −1.96[c]
12d	0.43	1.22	−1.35 to −1.98[c]
4a	0.45	1.35, 1.65	−1.43 to −2 [c]
4b	0.4	1.23	−1.45 to −2[c]

[a] Experimental conditions: CH_2Cl_2–CH_3CN 2:1 (v:v), Et_4NBF_4 (0.1 M); concentration in electro-active compound: 5×10^{-3} M; 2 mm^2 glassy carbon working electrode; SCE reference; 100 mV s^{-1} sweep rate, 20 °C. [b] Composed of 3 reversible waves. [c] Composed of 3 irreversible waves.



Scheme 7

5.00 (2H, m, $Cp_{subst.}$), 7.50 (8H, s, aromatics), 10.18 (2H, s, CHO); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 69.2, 71.25, 72.3, 89.95, 91.4, 122.0, 129.5, 131.45, 136.55, 192.7; IR ($CHCl_3$, cm^{-1}) 1662 (CO); MS (EI) m/z 121 (33%), 262 (30), 602 (M, 100%); HR-MS m/z calcd for $C_{36}H_{26}Fe_2O_2$: 602.0632; found: 602.0631.

(R_{Fc},$R_{Fc'}$,$R_{Fc''}$,$R_{Fc'''}$,$R_{Fc''''}$,$R_{Fc'''''}$)-Hexa[4-(α-formylferrocenyl)-1-phenyl]benzene, 8a. A dry Schlenk tube was charged with alkyne **7a** (0.83 mmol, 500 mg) and $Co_2(CO)_8$ (0.083 mmol, 30 mg) under argon. Freshly distilled dioxane (10 ml) was injected and the solution was refluxed overnight. After evaporation of the solvent, the crude reaction mixture was purified by flash chromatography on silica gel (diethyl ether–cyclohexane–CH_2Cl_2, 2:1:1). Cyclotrimer **8a** was isolated as an orange solid (425 mg, 85% yield). M.p. (decomp.) $>250\,^{\circ}C$, $[\alpha]_D^{23}$ +450 (c 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.04 (30H, s, Cp), 4.56 (6H, m, $Cp_{subst.}$), 4.66 (6H, m, $Cp_{subst.}$), 4.85 (6H, m, $Cp_{subst.}$), 6.91 (12H, d, $J = 7.7$ Hz, aromatics), 7.12 (12H, d, $J = 7.7$ Hz, aromatics), 9.96 (6H, s, CHO); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 68.5, 71.05, 71.95, 74.55, 77.2, 91.9, 128.1, 131.25, 133.25, 139.45, 140.1, 193.65; IR ($CHCl_3$, cm^{-1}) 1665.5 (CO); FAB-MS m/z 1807.2 (M^+).

(R_{Fc},$R_{Fc'}$,$R_{Fc''}$,$R_{Fc'''}$,$R_{Fc''''}$,$R_{Fc'''''}$)-Hexa{(*E*)-4-[2′-(α-formylferrocenyl)1′-vinyl]-1-phenyl}benzene, 8b. Cyclotrimer **8b** was synthesised using the same procedure as for **8a** with 200 mg (0.3 mmol) of **7b**. Yield: 85%; m.p. (decomp.) $>250\,^{\circ}C$, $[\alpha]_D^{23}$ −625 (c 0.064, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.16 (30H, s, Cp), 4.57 (6H, t, $J = 2.5$ Hz, $Cp_{subst.}$), 4.76 (6H, m, $Cp_{subst.}$), 4.87 (6H, m, $Cp_{subst.}$), 6.63 (6H, d, $J = 16$ Hz, H_{alkene}), 6.85 (12H, d, $J = 8$ Hz, aromatics), 7.05 (12H, d, $J = 8$ Hz, aromatics), 7.20 (6H, d, $J = 16$ Hz, H_{alkene}), 10.09 (6H, s, CHO); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 70.1, 71.45, 72.55, 77.2, 86.4, 122.75, 124.9, 129.55, 131.7, 134.1, 139.85, 140.15, 193.4; IR ($CHCl_3$, cm^{-1}) 1672 (CO); FAB-MS m/z 1963.1 (M^+).

(R_{Fc},$R_{Fc'}$)-1,2-Bis{4′-[α-(1″,3″-benzodithiol-2″-ylferrocenyl)-vinyl]-1′-phenyl}acetylene, 1a. In a dry Schlenk tube were placed the alkyne **7a** (0.166 mmol, 100 mg) and the phosphonate **9** (0.498 mmol, 145 mg). THF (10 ml) was added and the solution cooled to 0 °C before the slow addition of *t*-BuOK (0.498 mmol, 56 mg) in 5 ml of THF. The heterogeneous solution was warmed to RT and stirred overnight. The mixture was quenched with water at 0 °C, extracted with CH_2Cl_2 and dried over $MgSO_4$. After evaporation of the solvent, the crude reaction mixture was purified by flash chromatography on silica gel (diethyl ether–CH_2Cl_2, 1:1). Monomer **1a** was isolated as an orange solid (100 mg, 69% yield). M.p. 105 °C, $[\alpha]_D^{23}$ +900 (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.94 (10H, s, Cp), 4.23 (2H, t, $J = 2.6$ Hz, $Cp_{subst.}$), 4.40 (2H, m, $Cp_{subst.}$), 4.64 (2H, m, $Cp_{subst.}$), 6.11 (2H, s, CH), 6.89–7.17 (16H, m, aromatics); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 66.95, 67.9, 69.35, 70.65, 81.3, 85.8, 89.85, 110.8, 121.0, 121.2, 121.6, 125.45, 125.75, 129.45, 129.55, 131.25, 135.45, 136.75, 138.75; HR-MS m/z calcd for $C_{50}H_{34}Fe_2S_4$: 874.0242; found: 874.0500.

(*E*,*E*,R_{Fc},$R_{Fc'}$)-1,2-Bis(4′-{2″-[α-(1‴,3‴-benzodithiol-2‴-ylferrocenylvinyl)]-1″-vinyl}-1′-phenyl)acetylene, 1b. Monomer **1b** was synthesised using the same procedure as for **1a** with 65 mg (0.1 mmol) of **7b** and 3 equiv. of phosphonate **9** and *t*-BuOK. Yield: 65%, m.p. (decomp.) $>220\,^{\circ}C$; $[\alpha]_D^{23}$ +853 (c 0.034, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.14 (10H, s, Cp), 4.44 (2H, br s, $Cp_{subst.}$), 4.65 (2H, br s, $Cp_{subst.}$), 4.81 (2H, br s, $Cp_{subst.}$), 6.35 (2H, s, CH), 6.72 (2H, d, $J = 15.6$ Hz, H_{alkene}), 6.90–7.50 (18H, m, aromatics + H_{alkene}); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 65.4, 66.3, 67.15, 70.75, 81.1, 89.15, 90.2, 110.15, 120.25, 121.0, 121.6, 125.5, 125.75, 125.75, 126.1, 126.35, 129.1, 130.1, 131.4, 131.9, 135.3, 136.74, 137.65, 138.3.

(R_{Fc},$R_{Fc'}$,$R_{Fc''}$,$R_{Fc'''}$,$R_{Fc''''}$,$R_{Fc'''''}$)-Hexa{4-[α-(1′,3′-benzodithiol-2′-ylferrocenylvinyl)]-1-phenyl}benzene, 2a. Cyclotrimer **2a** was synthesised using the same procedure as for **1a** with 80 mg (0.0443 mmol) of **8a** and 10 equiv. of phosphonate **9** and *t*-BuOK. Yield: 52%, m.p. 212 °C, $[\alpha]_D^{23}$ +1747 (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.14 (30H, s, Cp), 4.41 (6H, t, $J = 2.5$ Hz, $Cp_{subst.}$), 4.53 (6H, m, $Cp_{subst.}$), 4.83 (6H, m, $Cp_{subst.}$), 6.31 (6H, s, CH), 7.05–7.30 (24H, m, aromatics); 7.51 (24H, s, aromatics); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 66.7, 67.45, 69.25, 70.55, 77.2, 81.1, 85.95, 111.8, 120.95, 121.4, 125.2, 125.5, 127.55, 128.7, 131.4, 135.1, 135.65, 136.9, 138.4, 140.35; FAB-MS m/z 2624.1 (M^+, 8%), 1312.0 (M^{2+}, 30%).

(R_{Fc},$R_{Fc'}$,$R_{Fc''}$,$R_{Fc'''}$,$R_{Fc''''}$,$R_{Fc'''''}$)-Hexa(4-{(*E*)-2′-[α-(1″,3″-benzodithiol-2″-ylferrocenylvinyl)]-1′-vinyl}-1-phenyl)benzene, 2b. Cyclotrimer **2b** was synthesised using the same procedure as for **1a** with 80 mg (0.041 mmol) of **8b** and 10 equiv. of phosphonate **9** and *t*-BuOK. Yield: 88%, m.p. (decomp.) $>220\,^{\circ}C$, $[\alpha]_D^{23}$ +1240 (c 0.088, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.06 (30H, s, Cp), 4.30 (6H, t, $J = 2.6$ Hz, $Cp_{subst.}$), 4.51 (6H, m, $Cp_{subst.}$), 4.63 (6H, m, $Cp_{subst.}$), 6.29 (6H, s, CH), 6.55 (6H, d, 15.9 Hz, H_{alkene}), 6.82 (6H, d, 15.9 Hz, H_{alkene}), 6.86 (12H, d, 8.1 Hz, aromatics), 6.99–7.22 (36 H, m, aromatics); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 65.1, 66.9, 68.3, 70.2, 81.75, 109.8, 120.95, 121.45, 123.85, 124.6, 125.3, 125.6, 127.6, 128.2, 129.0, 129.35, 131.85, 134.6, 135.5, 136.75, 139.5, 140.25.

(R_{Fc})-(α-*p*-Methoxyphenyl)-1,3-benzodithiol-2-ylferrocenylvinyl, 13. This compound was synthesised using the same

procedure as for **1a** with 200 mg (0.625 mmol) of (R_{Fc})-(α-*p*-methoxyphenyl)ferrocenecarboxaldehyde[20] and 1.5 equiv. of phosphonate **9** and *t*-BuOK. Yield: 100%, m.p. 126 °C, $[\alpha]_D^{23}$ +2209 (*c* 0.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.83 (3H, s, Me), 4.13 (5H, s, Cp), 4.35 (1H, t, *J* = 2.3 Hz, $Cp_{subst.}$), 4.45 (1H, br s, $Cp_{subst.}$), 4.79 (1H, br s, $Cp_{subst.}$), 6.27 (1H, s, CH), 6.89 (2H, d, *J* = 8.7 Hz, aromatics), 7.00–7.30 (4H, m, aromatics), 7.44 (2H, d, *J* = 8.7 Hz, aromatics); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 55.3, 66.2, 67.35, 69.25, 70.45, 81.1, 87.0, 111.35, 113.5, 120.9, 121.55, 125.4, 125.7, 128.7, 130.05, 130.7, 135.5, 136.85, 158.3; HR-MS *m*/*z* calcd for $C_{25}H_{20}FeOS_2$: 456.0305; found: 456.0298.

(S_{Fc})-(α-*p*-Methoxyphenyl)ethylferrocene, 14. To a solution of (R_{Fc})-(α-*p*-methoxyphenyl)ferrocenecarboxaldehyde (2 mmol, 640 mg) in 40 ml of diethyl ether at 0 °C was slowly added a 3 M solution of MeMgBr in diethyl ether (4 mmol, 1.33 ml). The reaction mixture was then warmed to RT and stirred for 3 h. After hydrolysis, the organic phase was washed with brine and dried over magnesium sulfate. The product was purified by flash chromatography (SiO_2, diethyl ether) to give 670 mg (100%) of the alcohol as an orange oil.

To a solution of $AlCl_3$ (4 mmol, 533.5 mg) in 20 ml of diethyl ether at 0 °C was added $LiAlH_4$ (6.6 mmol, 250.5 mg) by portions; the mixture was warmed to RT and stirred for 1 h. The mixture was cooled again to 0 °C and a solution of the alcohol (2 mmol, 670 mg) in 20 ml of diethyl ether was slowly added. The reaction mixture was warmed to RT and stirred overnight. The reaction mixture was slowly added to a mixture of ice and 2 M HCl. The product was extracted with diethyl ether, washed with brine and dried over magnesium sulfate. The product was purified by flash chromatography (SiO_2, diethyl ether) to yield an orange solid (590 mg, 92% yield). M.p. 60 °C, $[\alpha]_D^{23}$ −75 (*c* 0.466, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.18 (3H, t, *J* = 7.4 Hz, C*H*$_3$–CH_2), 2.54 (2H, dq, 7.6 Hz, C*H*$_2$–CH_3), 3.82 (3H, s, O–CH_3), 4.05 (5H, s, Cp), 4.13 (1H, t, *J* = 2.4 Hz, $Cp_{subst.}$), 4.18 (1H, t, *J* = 2 Hz, $Cp_{subst.}$), 4.32 (1H, t, *J* = 2.1 Hz, $Cp_{subst.}$), 6.86 (2H, d, *J* = 8.7 Hz, aromatics), 7.45 (2H, d, *J* = 8.7 Hz, aromatics); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.85, 21.35, 55.2, 65.8, 67.65, 68.7, 69.75, 86.6, 88.75, 113.3, 130.0, 130.95, 157.85; HR-MS *m*/*z* calcd for $C_{19}H_{20}FeO$: 320.0864; found: 320.0868.

(*E*)-4-Methyl-4′-ferrocenylvinyl-2,2′-bipyridine, 16[21]. To a suspension of NaH (6 mmol, 144 mg) in 5 ml of THF was added slowly a mixture of ferrocenecarboxaldehyde (0.87 mmol, 186 mg) and phosphine oxide **10** (1.15 mmol, 436 mg) in 20 ml of THF; the mixture was heated at reflux overnight. After cooling to RT the reaction mixture is cautiously hydrolysed at 0 °C with 10 ml of water, then the product was extracted with dichloromethane and dried over magnesium sulfate. The product was purified by flash chromatography (SiO_2, ethyl acetate) to give a red solid (260 mg, 78% yield). M.p. 173 °C, ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.43 (3H, s, CH_3), 4.13 (5H, s, Cp), 4.34 (2H, AA′XX′ system, *J* = 1.7 Hz, $Cp_{subst.}$), 4.49 (2H, AA′XX′ system, *J* = 1.7 Hz, $Cp_{subst.}$), 6.68 (1H, d, *J* = 16.1 Hz, H_{alkene}), 7.14 (1H, d, *J* = 5 Hz, H_5), 7.26 (1H, d, *J* = 4.8 Hz, $H_{5'}$), 7.27 (1H, d, *J* = 16.1 Hz, H_{alkene}), 8.23 and 8.41 (2H, 2 br s, $H_{3,3'}$), 8.56 (2H, 2 d, *J* = 5.1 and 4.8 Hz, $H_{6,6'}$); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 21.15, 67.4, 69.35, 69.75, 81.65, 117.3, 120.35, 122.0, 123.3, 124.7, 132.6, 146.1, 148.15, 148.85, 149.45, 156.0, 156.45; HR-MS *m*/*z* calcd for $C_{23}H_{20}FeN_2$: 380.0976; found: 380.0945.

Bis(4,4′-di-*tert*-butyl-2,2′-bipyridine)-(4-methyl-4′-ferrocenylvinyl-2,2′-bipyridine)ruthenium(II) dihexafluorophosphate, 17b. The ligand **16** (0.263 mmol, 100 mg) and *cis*-dichlorobis(4,4′-di-*tert*-butyl-2,2′-bipyridine)ruthenium(II) (0.395 mmol, 280 mg) were dissolved in 16.5 ml of a mixture of ethanol–water (10:1) and the mixture was refluxed overnight. After cooling to RT a saturated solution of NH_4PF_6 (1.315 mmol, 214 mg) was added. After 10 min the red precipitate was filtered, washed with water and ether and dried under vacuum. The product was purified by flash chromatography (SiO_2, acetonitrile–water–KNO_{3sat} 47:2.5:0.5). The major fraction was isolated, concentrated, and dissolved in a minimum volume of acetonitrile, then precipitated by addition of a saturated solution of NH_4PF_6. After filtration and washing, the product was dried in vacuum overnight to give a red solid (300 mg, 87% yield). M.p. (decomp.) > 250 °C, ^{1}H NMR (CD_3CN/$NaHSO_3$ in D_2O, 200 MHz) δ 1.39 (36 H, s, *t*-Bu), 2.55 (3H, s, Me), 4.18 (5H, s, Cp), 4.46 (2H, s, $Cp_{subst.}$), 4.62 (2H, s, $Cp_{subst.}$), 6.80 (1H, d, *J* = 16.1 Hz, H_{alkene}), 7.20–7.70 (13H, m, H_{alkene} + H_{bipy}), 8.47 (6H, br s, H_{bipy}); ^{13}C NMR (CD_3CN/$NaHSO_3$ in D_2O, 63 MHz) δ 21.0, 30.2, 36.05, 68.75, 70.25, 71.45, 81.7, 119.95, 121.45, 122.15, 124.0, 125.3, 128.9, 137.85, 141.3, 150.8, 151.25, 151.49, 151.5, 153.9, 157.6, 163.05; ESI-MS *m*/*z* 509.2 (M^{2+}, 100%); 1163.3 ($M^{2+} + PF_6^-$, 9%).

Bis(2,2′-bipyridine)-(4-methyl-4′-ferrocenylvinyl-2,2′-bipyridine)ruthénium(II) dihexafluorophosphate, 17a[20]. This complex was synthesised using the same procedure as for **17b** from **16** (0.156 mmol, 60 mg), *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) (0.19 mmol, 92 mg), 10 ml of an ethanol–water (10:1) mixture and NH_4PF_6 (0.347 mmol, 57 mg). After purification the complex **17a** was isolated as a red powder (130 mg, 77% yield). M.p. (decomp.) > 250 °C, ^{1}H NMR (CD_3CN, 250 MHz) δ 2.55 (3H, s, CH_3), 4.20 (5H, s, Cp), 4.48 (2H, br s, $Cp_{subst.}$), 4.63 (2H, br s, $Cp_{subst.}$), 6.81 (1H, d, *J* = 16.1 Hz, H_{alkene}), 7.25 (1H, d, *J* = 5.1 Hz, H_{bipy}), 7.31 (1H, d, *J* = 5.4 Hz, H_{bipy}), 7.40 (4H, m, H_{bipy}), 7.53 (2H, m, H_{bipy}), 7.58 (1H, d, *J* = 16.1 Hz, H_{alkene}), 7.74 (3H, m, H_{bipy}), 7.85 (1H, d, *J* = 5.1 Hz, H_{bipy}), 8.06 (4H, t, *J* = 7.6 Hz, H_{bipy}), 8.48 and 8.51 (6H, 2 br s, H_{bipy}); ^{13}C NMR (CD_3CN, 63 MHz) δ 21.25, 69.05, 70.5, 71.7, 120.65, 121.65, 124.15, 125.2, 126.0, 128.45, 129.15, 138.35, 128.6, 148.15, 151.4, 151.65, 152.3, 152.5, 152.6, 157.6, 157.9, 158.0, 165; ESI-MS *m*/*z* 397.0 (M^{2+}, 100%); 939.0 ($M^{2+} + PF_6^-$, 14%).

(*E*,*E*,R_{Fc},$R_{Fc'}$)-1,2-Bis{4′-[α-(4″-methyl-4‴-vinyl-2″,2‴-bipyridine)ferrocenyl]-1′-phenyl}acetylene, 11a. This compound was synthesised using the same procedure as for **16** with 430 mg of **7a** (0.72 mmol), 4 equiv. of phosphine oxide (2.86 mmol, 460 mg) and 16 equiv. of NaH (11.5 mmol, 276 mg). Yield: 82%, m.p. 144 °C, $[\alpha]_D^{23}$ +848 (*c* 0.25, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.43 (6H, s, CH_3), 4.13 (10H, s, Cp), 4.49 (2H, t, *J* = 2.2 Hz, $Cp_{subst.}$), 4.65 (2H, br s, $Cp_{subst.}$), 4.77 (2H, br s, $Cp_{subst.}$), 6.83 (2H, d, *J* = 16.1 Hz, H_{alkene}), 7.14 and 7.32 (4H, 2 d, *J* = 4.8 and 5.1 Hz, $H_{5,5'}$), 7.45 (2H, d, *J* = 16.1 Hz, H_{alkene}), 7.55 (8H, s, aromatics), 8.23 and 8.36 (4H, 2 br s, $H_{3,3'}$), 8.57 (4H, 2 d, *J* = 4.8 and 5.1 Hz, $H_{6,6'}$); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 21.2, 65.2, 69.05, 70.95, 71.7, 80.05, 87.95, 89.9, 118.2, 119.95, 121.4, 122.05, 124.75, 124.8, 129.45, 131.05, 131.4, 138.45, 146.05, 148.15, 148.9, 149.4, 155.95, 156.7. HR-MS *m*/*z* calcd for $C_{60}H_{46}Fe_2N_4$: 934.2421; found: 934.2425.

(*E*,*E*,*E*,*E*,R_{Fc},$R_{Fc'}$)-1,2-Bis(4′-{2″-[α-(4‴-methyl-4⁗-vinyl-2‴,2⁗-bipyridine)ferrocenyl]-1″-vinyl}-1′-phenyl)acetylene, 11b. This compound was synthesised using the same procedure as for **16** with 327 mg of **7b** (0.5 mmol), 4 equiv. of phosphine oxide (1.5 mmol, 576 mg) and 16 equiv. of NaH (6 mmol, 144 mg). Yield: 85%, m.p. 115 °C, $[\alpha]_D^{23}$ +250 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.48 (6H, s, Me), 4.14 (10H, s, Cp), 4.53 (2H, m, $Cp_{subst.}$), 4.78 (4H, m, $Cp_{subst.}$), 6.80 (2H, d, *J* = 16 Hz, H_{alkene}), 6.81 (2H, d, *J* = 15.9 Hz, H_{alkene}), 7.15–7.25 (4H, m, H_{alkene} + $H_{5or5'}$), 7.38 (2H, d, *J* = 5 Hz, $H_{5or5'}$), 7.52 (8H, s, aromatics); 7.56 (2H, d, *J* = 16 Hz,

H_{alkene}), 8.34 and 8.57 (4H, 2 s, $H_{3,3'}$), 8.62 (4H, 2 d, $J = 4.7$ and 5 Hz, $H_{6,6'}$); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 21.15, 66.8, 66.9, 69.9, 70.55, 81.15, 83.1, 90.55, 117.6, 120.45, 121.75, 122.1, 124.75, 125.5, 125.95, 127.15, 130.3, 131.9, 137.45, 146.0, 148.2, 148.85, 149.45, 155.9, 156.55; HR-MS m/z calcd for $C_{64}H_{50}Fe_2N_4$: 986.2734; found: 986.2738.

Complex 12a. The product **11a** (0.2 mmol, 187 mg) and *cis*-dichlorobis(4,4′-di-*tert*-butyl-2,2′-bipyridine)ruthenium(II) (0.6 mmol, 431 mg) were dissolved in 44 ml of ethanol–water (10:1) and the mixture was refluxed overnight. After cooling to RT a saturated solution of NH_4PF_6 (1 mmol, 163 mg) was added. After 10 min the red precipitate was filtered, washed with water and ether and dried under vacuum. The product was purified by flash chromatography (SiO_2, acetonitrile–water–KNO_{3sat} 47:2.5:0.5). The major fraction was isolated, concentrated, dissolved in a minimum volume of acetonitrile and then precipitated by addition of a saturated solution of NH_4PF_6. After filtration and washing, the product was dried in vacuum overnight to give a red solid (210 mg, 38% yield). M.p. (decomp.) $>250\,^{\circ}C$, $[\alpha]_D^{23}$ +818 (c 0.044, CH_3CN); ^1H NMR ($CD_3CN/NaHSO_3$ in D_2O, 250 MHz) δ 1.39 (72 H, s, *t*-Bu), 2.53 (6H, s, Me), 4.17 (10H, 2 s, Cp), 4.64 (2H, br, $Cp_{subst.}$), 4.80 (2H, br s, $Cp_{subst.}$), 4.92 (2H, br s, $Cp_{subst.}$), 6.94 (2H, d, $J = 15.5$ Hz, H_{alkene}), 7.23 (2H, d, $J = 5.5$ Hz, H_{bipy}), 7.25–7.75 (32 H, m, aromatics + H_{alkene} + H_{bipy}), 8.46 (12H, s, H_{bipy}); ^{13}C NMR ($CD_3CN/NaHSO_3$ in D_2O, 63 MHz) δ 21.05, 30.25, 36.05, 67.5, 70.65, 71.8, 74.6, 78.05, 80.05, 86.55, 89.5, 120.85, 122.2, 123.0, 124.0, 124.2, 125.3, 125.7, 129.0, 129.45, 130.2, 130.4, 130.6, 132.05, 132.3, 135.0, 147.25, 150.75, 151.55, 157.6, 164.0; ESI-MS m/z 553.2 (M^{4+}, 20%); 785.6 ($M^{4+} + PF_6^-$, 100%).

Complex 12b. This complex was synthesised using the same procedure as for **12a** from **11b** (0.056 mmol, 56 mg), *cis*-dichlorobis(4,4′-di-*tert*-butyl-2,2′-bipyridine)ruthenium(II) (0.14 mmol, 100 mg), 11 ml of a ethanol–water (10:1) and NH_4PF_6 (0.28 mmol, 46 mg). After purification complex **12b** was isolated as a red powder (70 mg, 44% yield). M.p. (decomp.) $>250\,^{\circ}C$, $[\alpha]_D^{23}$ +250 (c 0.016, CH_3CN); ^1H NMR ($CD_3CN/NaHSO_3$ in D_2O, 200 MHz) δ 1.43 (72H, s, *t*-Bu), 2.60 (6H, s, Me), 4.18 (10H, s, Cp), 4.68 (2H, t, $J = 2.5$ Hz, $Cp_{subst.}$), 4.92 (2H, m, $Cp_{subst.}$), 4.98 (2H, m, $Cp_{subst.}$), 6.94 (2H, d, $J = 15.9$ Hz, H_{alkene}), 6.96 (2H, d, $J = 16$ Hz, H_{alkene}), 7.27 (2H, d, $J = 6.2$ Hz, H_{bipy}), 7.30–7.75 (32H, m, aromatics + H_{alkene} + H_{bipy}), 7.87 (2H, d, $J = 16.2$ Hz, H_{alkene}), 8.49 (8H, s, H_{bipy}), 8.54 (2H, s, H_{bipy}), 8.60 (2H, s, H_{bipy}); ^{13}C NMR ($CD_3CN/NaHSO_3$ in D_2O, 63 MHz) δ 21.05, 30.2, 36.0, 67.55, 68.3, 71.5, 71.8, 81.25, 84.7, 90.95, 120.55, 122.0, 122.1, 122.8, 124.25, 125.3, 126.75, 126.95, 127.5, 128.95, 132.5, 135.4, 138.9, 147.35, 150.75, 151.2, 151.5, 157.5, 157.6, 157.85, 163.05; ESI-MS m/z 565.5 (M^{4+}, 21%); 802.3 ($M^{4+} + PF_6^-$, 100%).

Complex 12c. This complex was synthesised using the same procedure as for **12a** from **11a** (0.107 mmol, 100 mg), *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) (0.268 mmol, 130 mg), 22 ml of ethanol–water (10:1) and NH_4PF_6 (1.07 mmol, 175 mg). After purification the complex **12c** was isolated as a red powder (90 mg, 36% yield). m.p. (decomp.) $>250\,^{\circ}C$, $[\alpha]_D^{23}$ +694 (c 0.11, CH_3CN); ^1H NMR (CD_3CN, 200 MHz) δ 2.54 and 2.58 (6H, 2 s, Me), 4.17 and 4.18 (10H, 2 s, Cp), 4.66 (2H, t, $J = 2.5$ Hz, $Cp_{subst.}$), 4.83 (2H, m, $Cp_{subst.}$), 4.97 (2H, m, $Cp_{subst.}$), 7.09 (2H, d, $J = 16$ Hz, H_{alkene}), 7.38 (2H, d, $J = 6$ Hz, H_{bipy}), 7.40–7.70 (20H, m, aromatics + H_{bipy}), 7.78 (2H, d, $J = 6.1$ Hz, H_{bipy}), 7.79 (2H, d, $J = 16.1$ Hz, H_{alkene}), 7.83 (2H, d, $J = 5.7$ Hz, H_{bipy}), 8.03 (6H, m, H_{bipy}), 8.10–8.25 (12H, m, H_{bipy}), 8.67 (2H, s, H_{bipy}), 8.79 (6H, m, H_{bipy}); ^{13}C NMR (CD_3CN, 63 MHz) δ 21.0, 30.2, 67.45, 70.9, 71.85, 73.2, 79.95, 89.0, 90.3, 120.8, 121.65, 123.0, 124.2, 124.9, 125.75, 128.2, 129.0, 130.45, 132.0, 136.05, 138.35, 139.5, 147.55, 151.1, 151.35, 151.8, 152.35, 157.25, 157.65, 157.75; ESI-MS m/z 440.1 (M^{4+}, 23%); 635.8 ($M^{4+} + PF_6^-$, 100%); 1026.1 ($M^{4+} + 2PF_6^-$, 67%); 2197.1 1 ($M^{4+} + 3PF_6^-$, 3%).

Complex 12d. This complex was synthesised using the same procedure as for **12a** from **11b** (0.061 mmol, 60 mg), *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) (0.152 mmol, 74 mg), 15 ml of ethanol–water (10:1) and NH_4PF_6 (0.61 mmol, 100 mg). After purification the complex **12d** was isolated as a red powder (47 mg, 32% yield). M.p. (decomp.) $>250\,^{\circ}C$, $[\alpha]_D^{23}$ +361 (c 0.036, CH_3CN); ^1H NMR (CD_3CN, 200 MHz) δ 2.58 (6H, s, Me), 4.17 (10H, 2 s, Cp), 4.66 (2H, br s, $Cp_{subst.}$), 4.91 (2H, br s, $Cp_{subst.}$), 4.97 (2H, br s, $Cp_{subst.}$), 6.92 (2H, d, $J = 16.2$ Hz, H_{alkene}), 6.94 (2H, d, $J = 16$ Hz, H_{alkene}), 7.15–7.95 (36H, m, aromatics + H_{alkene} + H_{bipy}), 8.06 (8H, t, $J = 7.4$ Hz, H_{bipy}), 8.54 (12H, m, H_{bipy}); ^{13}C NMR (CD_3CN, 63 MHz) δ 21.0, 21.2, 61.75, 67.5, 68.2, 71.45, 81.1, 84.7, 89.45, 90.7, 120.6, 122.05, 122.65, 124.3, 124.85, 125.7, 126.85, 127.45, 128.2, 128.95, 130.05, 131.9, 132.4, 135.6, 138.3, 139.7, 147.6, 151.1, 151.35, 151.8, 152.2, 152.3, 157.25, 157.7 ESI-MS m/z 505 (100%); 1155 (80%).

Cyclotrimer 4a. A dry Schlenk tube was charged with complex **12a** (0.036 mmol, 100 mg) and $Co_2(CO)_8$ (0.0036 mmol, 1.3 mg) under argon. Freshly distilled 1,2-dichloroethane (4 ml) and dioxane (1 ml) were injected and the solution was refluxed for 12 h. After evaporation of the solvent, the crude reaction mixture was purified by flash chromatography (SiO_2, acetonitrile–water–KNO_{3sat} 47:2.5:0.5). The major fraction was isolated, concentrated, dissolved in a minimum volume of acetonitrile and precipitated by addition of a saturated solution of NH_4PF_6. After filtration and washing, the product was dried in vacuum overnight to give a red solid (70 mg, 70% yield). M.p. (decomp.) $>300\,^{\circ}C$, $[\alpha]_D^{23}$ +1438 (c 0.016, $CHCl_3$). ^1H NMR ($CD_3CN/NaHSO_3$ in D_2O, 250 MHz) δ 1.43 (216H, br s, *t*-Bu), 2.64 (18H, br s, CH_3), 3.70–4.10 (36H, m, Cp + 1 $Cp_{subst.}$), 4.30 (6H, m, $Cp_{subst.}$), 4.55 (6H, m, $Cp_{subst.}$), 6.67 (8H, m), 6.87 (6H, m), 7.12 (18H, br s), 7.20–7.70 (50H, m), 8.20 and 8.26 (4H, 2 br s), 8.49 (22H, br s); FAB-MS m/z 2649.3 (M^{3+}, 13%, calcd. 2648.1), 1950.6 (M^{4+}, 100%, calcd. 1949.8), 1531.4 (M^{5+}, 67%, calcd. 1530.9), 1251.5 (M^{6+}, 32%, calcd. 1251.6), 1052.8 (M^{7+}, 4%, calcd. 1052.1).

Cyclotrimer 4b. This complex was synthesised using the same procedure as for **4a** with 75 mg of **12b** (0.026 mmol) with $Co_2(CO)_8$ (0.0026 mmol, 0.9 mg). After purification complex **4b** was isolated as a red powder (40 mg, 53% yield). M.p. (decomp.) $>300\,^{\circ}C$, $[\alpha]_D^{23}$ +2500 (c 0.006, $CHCl_3$); ^1H NMR ($CD_3CN/NaHSO_3$ in D_2O, 200 MHz) δ 1.40 (216 H, br s, *t*-Bu), 2.59 (18H, s, CH_3), 3.98 (30H, s, Cp), 4.38 (6H, m, $Cp_{subst.}$), 4.67 (6H, m, $Cp_{subst.}$), 4.75 (6H, m, $Cp_{subst.}$), 6.55–7.70 (94 H, m), 8.47 (26H, s); FAB-MS m/z 1986.9 (M^{4+}, 62%, calcd. 1987.3), 1561.5 (M^{5+}, 100%, calcd. 1560.9), 1277.4 (M^{6+}, 65%, calcd. 1276.6), 1075.1 (M^{7+}, 20%, calcd. 1073.5).

Cyclic voltammetry

Cyclic voltammetry measurements were carried out in dry and oxygen-free solvents (CH_2Cl_2 and acetonitrile) with 0.1 M tetrabutylammonium perchlorate (TBAP) or tetraethylammonium tetrafluoroborate (Et_4NBF_4) as the supporting electrolyte and with ~0.001 M substrate under a nitrogen inert gas atmosphere. A conventional three-electrode setup was used with a platinum disk working electrode and an Ag/AgCl pseudo-reference electrode. Digital simulation of the CVs for

some products was done with the kinetic program COOL (provided by EG & G Priceton Applied Research, Oak Ridge, TN, USA).

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