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PAPER

The synthesis and characterisation of novel ferrocenyl polyphenylenes†

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This work describes the synthesis and characterisation of a new series of polyphenylenes with up to four ferrocenyl moieties. The synthetic route involves the preparation of a number of novel precursors. Cyclopentadienones, generated from the two-fold Knoevenagel condensation of di-ferrocenyl propanones and diketones, are used in [2 + 4] Diels–Alder cycloadditions with appropriately substituted acetylenes. **13** is amongst the compounds isolated. It is the largest ferrocenyl-supported polyaromatic hydrocarbon (PAH) to date. Prepared *via* a Sonogashira cross-coupling reaction between ethynyl-Fc and iodo-HBC, it comprises a hexa-*peri*-hexabenzocoronene (HBC) core linked *via* acetylene to a ferrocenyl unit (Fc). The electrochemical and absorption properties of the ferrocenyl-polyphenylenes and the fully conjugated **13** are discussed. The NLO data for **13**, determined by hyper Rayleigh scattering techniques, are compared to those of similar fulleryl-based compounds in the literature.

Introduction

As a robust organometallic electron-donor group with well-established substitution chemistry[1] the ferrocenyl-moiety has been incorporated into new molecular materials exhibiting non-linear optical (NLO)[2] and ferromagnetic properties.[3] The bulk properties of a molecular material can be heavily influenced in the solid-state by its packing arrangement. For this reason, compounds combining a ferrocene donor and a planar polycyclic aromatic hydrocarbon (PAH), capable of π-stacking, are of considerable interest. PAHs are useful as linking groups in donor–acceptor organometallic systems because they are planar, relatively rigid with a fixed geometry and have various isomeric positions through which organometallic moieties may be bound. Their highly delocalised π-systems with small HOMO–LUMO energy separations and low vacant π*-orbitals can facilitate electronic communication between donors and acceptors. Although large polycyclic materials incorporating over 200 carbon atoms have been characterised, very few of these systems are organometallic. Known examples include Bunz's cobalt-containing ethynylated cyclobutadienes,[4–6] η^6-tricarbonyl chromium[7] and η^6-[Rh(COD)]$^+$ hexa-*peri*-hexabenzocoronene (HBC)[8] and HBCs incorporating σ-bonded Pt(II) acetylides.[9]

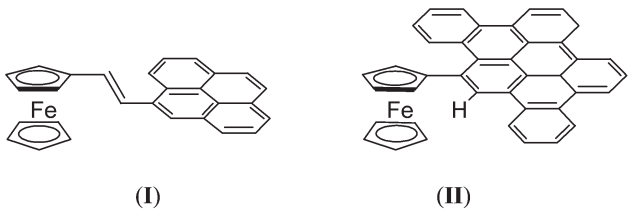

Fig. 1 The structures of the two known PAHs incorporating a ferrocene moiety 1,2-ferrocenyl-pyrenyl-ethene (**I**) and tetra-*peri*-benzo-*peri*-ferrocenyl-coronene (**II**).

To date there are just two compounds reported where ferrocene is attached to an all-benzenoid PAH, one of which comprises four fused benzene rings,[3] the other eight (Fig. 1).[10] Both come some way short of the thirteen fused benzene rings found in HBC (Fig. 2). The L-shaped 1,2-ferrocenyl-pyrenyl-ethene (**I**) has fascinating solid state electrical conductivity properties[3] whereas (**II**) with a single bond between the ferrocene moiety and the PAH fragment offers limited communication between the two end groups (Fig. 1).[10]

To combine the desirable features of both **I** and **II** we decided to increase the size of the PAH platform and to introduce an acetylene linker as an active pathway for electronic communication. Known ferrocenyl-acetylenes have been shown to have considerable potential in NLO, catalysis, as models of charge transfer and in the synthesis of more complex molecules with well-defined magnetic and electronic properties.[4,11–13] Given these considerations, **13** became a desirable target molecule (Fig. 2).

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†Electronic supplementary information (ESI) available: ^{1}H NMR (400 MHz) spectra recorded in $CDCl_3$ of **4**, **7**, **8**, **9**, **10**, **11**, **12**, iodo-HBC and 1,2-bis(*p*-ferrocenylphenyl)acetylene. The experimental (+)-MALDI-TOF spectra of **13** and (MH)$^+$ simulated isotopic distribution pattern. Schematic and experimental details for the total synthesis of 1,2-bis(*p*-ferrocenylphenyl)acetylene. Tabulated electronic charge of the ethyne, cyclopentadienyl (Cp), ferrocence and HBC components, ethynyl ferrocene and methyl derivative of **13**. See DOI: 10.1039/c2dt30542a

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Results and discussion

The ferrocene moiety was incorporated into the polyphenylene systems by synthesising a library of novel ferrocene-containing precursors, suitable for subsequent [2 + 4] Diels–Alder cycloaddition and conversion to aromatic PAHs *via* cyclodehydrogenation. The synthesised molecules contained up to four ferrocene units and in some cases nitrogen heteroatoms to aid solubility, and/or electron-rich methoxy groups.[14,15] It was hoped that such derivatisation would yield highly conjugated systems with moderately electron-donating and electron-accepting regions.

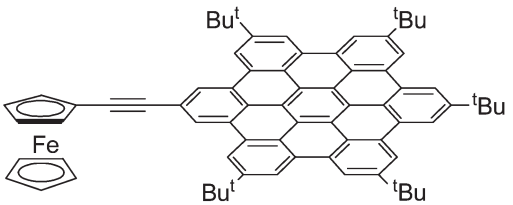
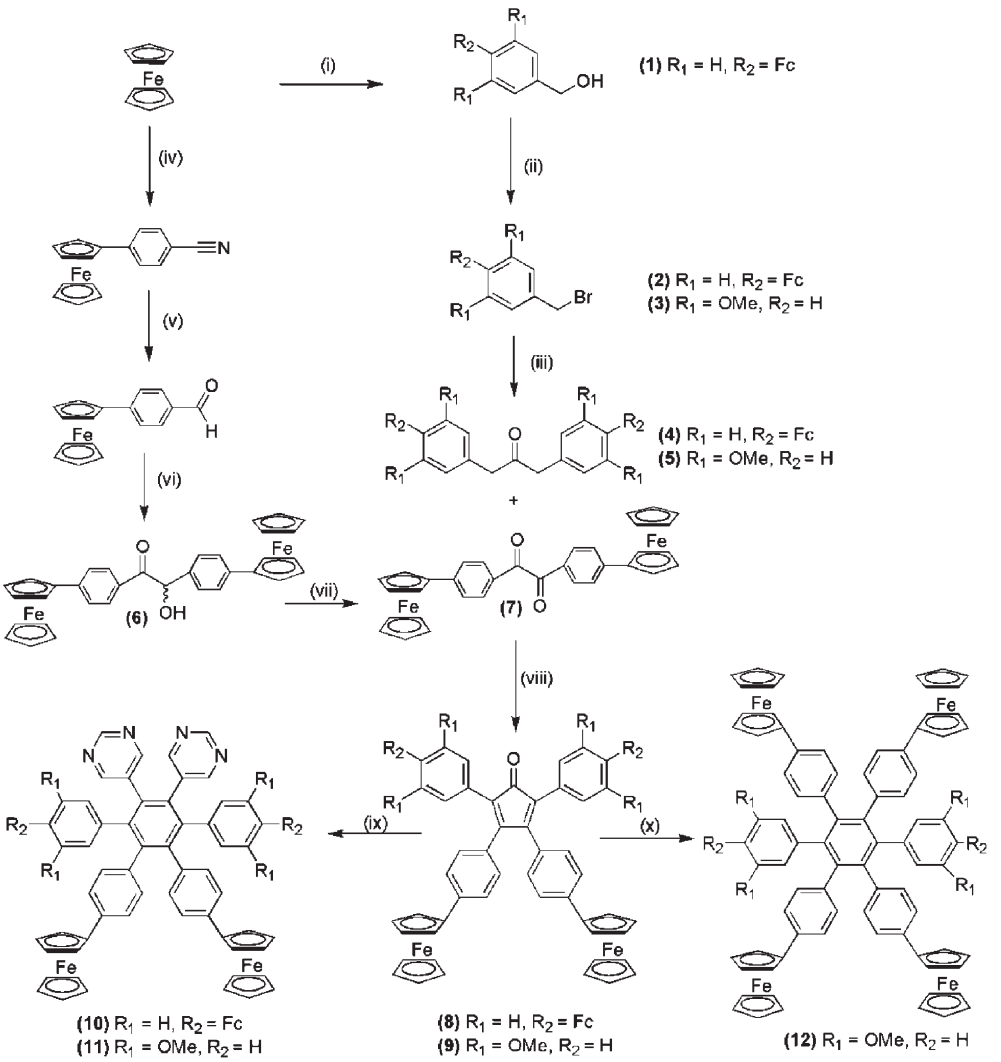


Fig. 2 Structure of 2-ethynylferrocenyl-5,8,11,14,17-penta-*tert*-butylhexa-*peri*-hexabenzocoronene (**13**).

Synthesis of heteroatom-containing polyphenylenes 10, 11 and 12

In order to incorporate multiple ferrocene moieties into the polyphenylene systems, di-ferrocenyl mono-ketone (**4**) was synthesised (Scheme 1). The initial step involved the synthesis of **1** *via* the diazotization reaction between ferrocene (FcH) and 4-aminobenzylalcohol. The bromination of the hydroxyl group was achieved using phosphorous tribromide in dichloromethane which yielded **2**, in almost quantitative yield. The new compound di-ferrocenyl ketone **4** was prepared by a bi-phasic, iron



Scheme 1 The synthetic route to polyphenylenes **10**, **11**, and **12**. (i) H_2SO_4/H_2O, sodium nitrite, 4-aminobenzylalcohol, HCl, Cu powder, 24 h, **1** (31%). (ii) PBr_3, CH_2Cl_2, 0 °C, 30 min, **2** (94%), (**3** purchased directly). (iii) $Ca(OH)_2$, $Bu_4N(HSO_4)$, $Fe(CO)_5$, CH_2Cl_2/H_2O, 6 h, **4** (58%), **5** (65%). (iv) H_2SO_4/H_2O, sodium nitrite, 4-aminobenzonitrile, HCl, Cu powder, 24 h, (35%). (v) DIBAL, toluene, RT, 6 h, (91%). (vi) NaCN, water/ethanol, reflux 1 h, **6** (59%). (vii) MnO_2, $CHCl_3$, reflux, 24 h, **7** (88%). (viii) KOH, C_2H_5OH/CH_2Cl_2, 18 h (**8**)/3 h (**9**), **8** (63%), **9** (64%). (ix) Dipyrimidylacetylene, benzophenone, 200 °C, 18 h, **10** (54%), **11** (58%). (x) 1,2-Bis(*p*-ferrocenylphenyl)acetylene, benzophenone, 190 °C, 18 h, **12** (18%).

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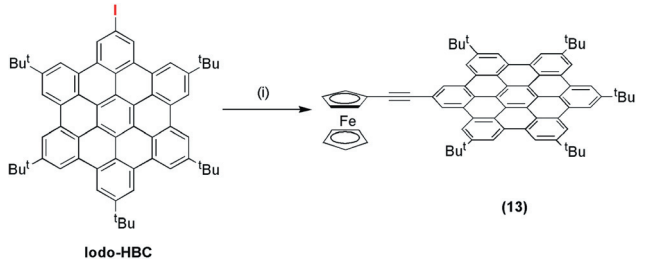

Scheme 2 Synthesis of **13** from iodo-HBC, (i) ethynyl ferrocene, $Pd(PPh_3)_4$, Et_3N–toluene (1 : 2), 70 °C, 18 h, (77%).

pentacarbonyl mediated coupling reaction. The methoxy-substituted 1,3-diaryl-2-propanone (**5**) was synthesised in a similar vein in 65% yield from the commercially available 3,-5-dimethoxybenzyl bromide (**3**). As well as the di-ferrocenyl mono-ketone (**4**) the di-ferrocenyl di-ketone (**7**) was also prepared. This was achieved in four steps from ferrocene as illustrated in Scheme 1. The first step involved a diazotization reaction between ferrocene and 4-aminobenzonitrile[16] to give 4-ferrocenylbenzonitrile (35% yield), for conversion to 4-ferrocenylbenzaldehyde in almost quantitative yield. The keto-alcohol **7** (also novel) was synthesised *via* the benzoin condensation of two molecules of 4-ferrocenylbenzaldehyde.

The two cyclopentadienones **8** and **9** were prepared *via* a two-fold Knoevenagel condensation reaction between **7** and the corresponding mono-ketones (**4** and **5**). Both condensations were carried out in ethanolic potassium hydroxide solutions. Cyclopentadienone **8** was found to be quite unstable as a solid and particularly unstable in solution. Polyphenylenes **10** and **11** were obtained as orange crystalline solids *via* the Diels–Alder [2 + 4]-cycloaddition of **8** and **9**, respectively, with dipyrimidyl acetylene.

To expand the library of possible compounds, 1,2-bis(*p*-ferrocenylphenyl)acetylene was successfully synthesised (Scheme S1, ESI†) using a route that differs from that published by Rathore *et al.*[17] and subsequently used in a [2 + 4] Diels–Alder cycloaddition with **9** to give tetra-ferrocenyl polyphenylene **12**.

Attempted cyclodehydrogenation of polyphenylenes 10, 11 and 12

Attempts to cyclodehydrogenate ferrocenyl polyphenylenes **10** and **11** to form planar, ring-closed systems were unsuccessful, yielding only black, insoluble and un-characterisable solids indicative of complete decomposition. In an attempt to improve on these results, polyphenylene **12** was produced (Scheme 1) to incorporate electron-donating methoxy groups which are known to activate C–C bond formation in cyclodehydrogenation reactions. This did not improve the outcome of the attempted cyclodehydrogenation which we believe to be a consequence of the partial oxidative decomposition by Cu(II) of the exposed Fe centre in tilted ferrocenyl moieties.[6,10]

Synthesis and spectroscopic characterisation of 2-ethynylferrocenyl-5,8,11,14,17-penta-*tert*-butylhexa-*peri*-hexabenzocoronene (13)

As a consequence of the unsuccessful cyclodehydrogenation of the ferrocene-containing **10**, **11** and **12**, a change of synthetic direction was required. Müllen *et al.*[18,19] amongst others[9,20] have shown that halogen atoms incorporated into PAH are labile enough to undergo palladium catalysed coupling reactions. It was decided to use iodo-HBC[9,20] which would benefit from the efficient nature of the Scholl reaction for the C–C bond formation in all-carbon polyphenylenes and simultaneously provide a predetermined site for the ferrocene moiety. Ethynyl ferrocene was synthesised according to literature procedures,[38] and was cross-coupled with iodo-HBC using Sonogashira methodology to give **13** (Scheme 2).

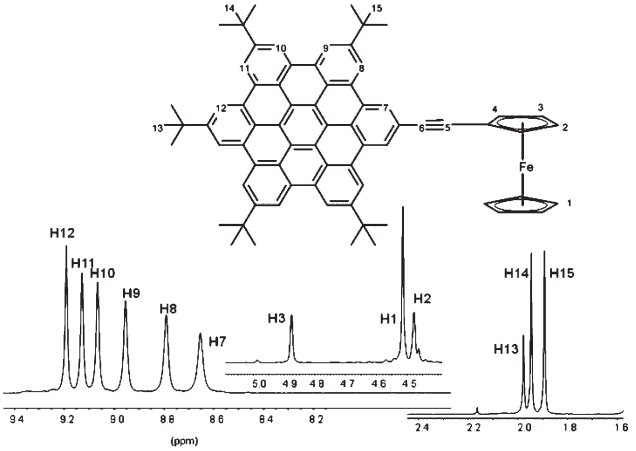

Fig. 3 ^{1}H NMR spectrum of **13** ($CDCl_3$, RT, 600 MHz).

The ^{1}H NMR spectrum of **13** consists of six well-defined singlets in the aromatic region due to the presence of a C_2 axis of symmetry which renders half the protons magnetically equivalent (Fig. 3). The ferrocenyl region exhibits the expected three signals corresponding to the two non-equivalent proton environments of the substituted cyclopentadienyl ring and the one proton environment of the protons on the unsubstituted cyclopentadienyl ring. In the aliphatic region three distinct signals are visible, integrating in the expected 1 : 2 : 2 ratio for the *tert*-butyl groups.

The ^{1}H NMR spectrum of **13** was readily assigned by various NOE and 2D experiments using the clearly discernible signal for the *tert*-butyl group H13. TOCSY experiments provided evidence for the long range interactions between protons on adjacent rings and allowed a full assignment of the spectrum.

Phenyl groups prefer to associate in either an edge-to-edge or face-to-face orientation (π–π stacking).[21] Such interactions have been the subject of a number of investigations[21–23] that have attempted to address the role of molecular geometry[22,23] and electrostatic factors in promoting aromatic association.[24–27] The ^{1}H NMR signals of the aromatic protons of **13** were found to be concentration dependent, especially the upfield protons H7, H8 and H9, which are closest to the ferrocene moiety (Fig. 4). At ambient temperature in $CDCl_3$ the chemical shift for H7 varied greatly from δ 8.90 ppm (7.40×10^{-3} M) to δ 9.19 ppm (0.06×10^{-3} M) suggesting a significant degree of molecular aggregation. It has been shown by Moore *et al.*[28] that ethynyl moieties can form π–π interactions with PAHs and macrocycles. The greatest overlap of π orbitals in **13** is likely to be in the region closest to the electron donating ferrocene, hence the movement of H7 in the ^{1}H NMR spectrum.

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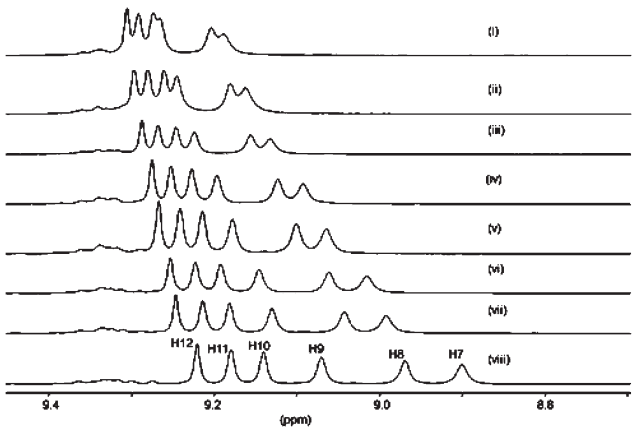

Fig. 4 The concentration dependence of the ^{1}H NMR aromatic signals of compound **13** ($CDCl_3$, RT, 600 MHz): (i) 0.06 mmol dm^{-3}, (ii) 0.12 mmol dm^{-3}, (iii) 0.23 mmol dm^{-3}, (iv) 0.46 mmol dm^{-3}, (v) 0.93 mmol dm^{-3}, (vi) 1.85 mmol dm^{-3}, (vii) 3.70 mmol dm^{-3}, (viii) 7.40 mmol dm^{-3}.

UV-Vis absorption spectroscopy of polyphenylenes 10–12 and Fc-ethynyl-HBC (13)

Electronic absorption spectra of ferrocene and substituted ferrocenes reveal that in ferrocene the metal centred d_z^2 orbital is generally the HOMO, a combination of the d_{xz} and d_{yz} is the LUMO and the LUMO + 1 has a proposed composition of the d_{xy} and $d_{x^2-y^2}$.[29,30] The absorption around λ 440 nm in ferrocene is thus assigned to the $^1E_{1g} \leftarrow {}^1A_{1g}$ [LUMO ← HOMO] ligand field (LF) transition and the higher energy band around λ 325 nm to the $^1E_{2g} \leftarrow {}^1A_{1g}$ [(LUMO + 1) ← HOMO] LF transition. Substitution of a Cp ring in ferrocene with conjugated acceptor groups is generally followed by drastic changes in absorption spectra.[29,30] LF, otherwise known as "d–d" transitions, in organometallics are highly covalent and the electronic transitions involving d-orbitals are sensitive to ligand binding.[31]

This weak d–d transition is evident between λ 440–445 nm (Table 1) for each of the ferrocenyl-polyaromatic molecules prepared here (polyphenylenes **10–12** and Fc-HBC (**13**)) with weak extinction coefficients indicative of the forbidden nature of the transition (ε = molar extinction coefficient, L mol^{-1} cm^{-1}). The minor variation in the energy of this band reveals the weak influence that the nature of the substituent has on the transition.

For PAHs the dominant π–π* transitions usually occur in the λ 300–420 nm region and are highly structured and well-resolved because of the delocalised and rigid nature of the molecular platform. The all-carbon HBC, hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (**14**) was synthesised[7] for direct comparison with **13** (Fig. 5).

The UV-Vis spectra of **13** and **14** have similar profiles; however as expected the absorptions in **13** are slightly red-shifted. Both spectra show the three-band profile (α, β and p), typical of aromatic hydrocarbons. The β-band appears at λ 366 nm and corresponds to the electronic interaction between the benzenoid rings of the PAH. The p-bands appear at λ 396 nm for **13** (5 nm red shift compared to **14**) and involve the localisation of the π-electrons in the excited state. The red-shifted band in **13** at λ 414 nm is assigned to the 0–0, ^{1}(π, π*) transition, with

Table 1 The UV-Vis data for ferrocene (FcH) and compounds **10–13** in toluene (~10^{-5} M)

Compound	λ_{max}/nm, (ε/L mol^{-1} cm^{-1} ×10^3)	Low energy d–d transition
FcH	325 (0.5)	439 (0.5)
10	355 (12.6)	443/5 (2.8)
11	354 (12.1)	440 (2.6)
12	350 *sh* (1.7)	445 (0.3)
13	334 (27.3), 350 (61.7), 366 (138.7), 396 (50.7), 414 (19.0)	*ca.* 440

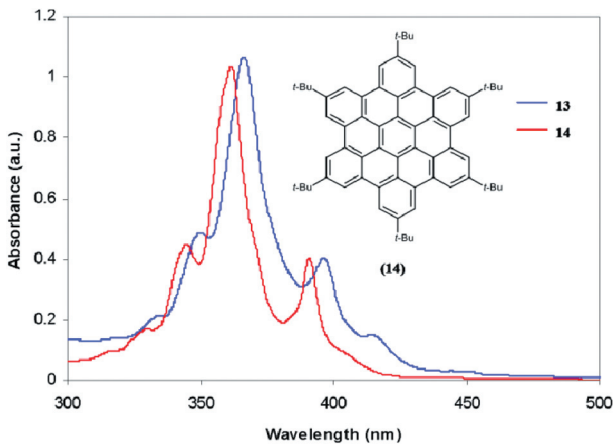

Fig. 5 The UV-Vis absorption spectra of **13** and **14** (inset) recorded in toluene (10^{-5} M).

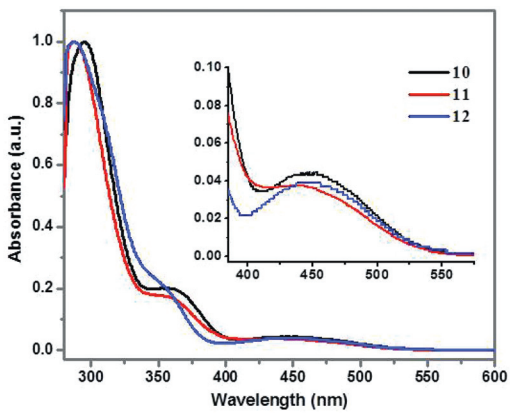

Fig. 6 Normalised UV-Vis absorption spectra of ferrocenyl-polyphenylenes **10–12** recorded in toluene (~10^{-5} M) with inset lower energy region.

enhanced molar absorptivity compared to **14** due to the lifting of molecular symmetry (D_{6h} to C_{2v}). The red-shift of these bands is indicative of an extension to the π-system of the HBC core, facilitated by the ethynyl linkage.

In contrast, the absorption spectra of polyphenylenes **10–12** are dominated by strong, high-energy absorption bands between λ 300–350 nm attributable to ππ* and nπ* transitions centred on the hexa-arylbenzene core (Fig. 6). Most probably the absence of effective conjugation between the ferrocenyl moiety and the polyphenylene occurs due to steric hindrance in the ground state.

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Table 2 Electrochemical data for ferrocenyl complexes[a]

Complex	$E°$/V	ΔE_p/mV
10	+0.03	169
11	−0.01	120
12	−0.06	114
13	+0.14	136
(**II**)	+0.04	70

[a] Redox potentials are given in CH_2Cl_2 solution (1 mM), using a platinum disc working electrode, Pt wire auxiliary electrode, Ag/Ag^+ reference electrode, 100 mV s^{-1} scan rate with 0.1 M Bu_4NPF_6 as supporting electrolyte (V *vs.* Fc/Fc^+). ΔE_p is given by ($E_{pa} - E_{pc}$).

This would impose a non-planar configuration of the bound Cp and the phenyl ring of the hexa-arylbenzene and consequently inefficient orbital overlap.

Electrochemistry

The ferrocene/ferrocenium redox couple represents a strictly reversible one-electron process, although in some cases reversibility is lowered by the subsequent decomposition of the electrogenerated ferrocenium species.[11] It gives information on any changes in the distribution of electron density and HOMO energies in a series of related compounds.[11] The relevant electrochemical data for polyphenylenes **10–12** and Fc-HBC (**13**) and for tetra-*peri*-benzo-*peri*-ferrocenyl-coronene (**II**) (structure presented in Fig. 1) as 1 mM dichloromethane solutions are compared in Table 2.

These compounds are electrochemically active and in each case, cyclic voltammetry in solution shows a single oxidation peak corresponding to the Fe(II)/Fe(III) redox couple. The oxidation potentials for **10–12** occur within the range −0.06 to +0.03 V, quite similar to ferrocene itself. This indicates that the electron density at the metal centre in these compounds, *i.e.* the energy of the HOMO, does not vary significantly upon changing substituents on the polyphenylene core. This is a consequence of the limited communication through the single carbon–carbon bond between the Fc moieties and the polyaromatic framework. Compounds **13** and (**II**) are usefully compared as both consist of a ferrocenyl moiety connected *via* a π-conjugated bridge to a fused aromatic platform. For (**II**) the fully reversible redox process was found to occur at +0.04 V (*vs.* Fc/Fc^+). This is anodically shifted compared to the *quasi*-reversible oxidation of **13** and is indicative of a comparative reduction in electron density at the iron centre in **13** relative to (**II**), with the result that its metal centre is comparatively more difficult to oxidise. The acetylene-HBC unit has a considerable influence on the redox properties of the Fe core which we explored using theoretical methods.

Theoretical considerations

To support the experimental findings and to verify the electron distribution within Fc-ethynyl-HBC (**13**), calculations were performed (Gaussian 09,[32] using the MO6 Hybrid functional[33] and 6-31G(d,p) basis set) on the component fragments (Fe, Cp, ethyne, and hexabenzocorenene (HBC)) in ferrocene, ethynylferrocene, and the methyl derivative of **13** (**methyl 13**). Consistent with its highly conjugated π-system HBC was found to have the highest HOMO and lowest LUMO of the fragments considered. Ferrocene had the next highest HOMO and the next lowest LUMO (with a significant part of the wavefunction on the Fe) and ethyne had the lowest HOMO and the highest LUMO. The energy of these frontier orbitals carried through to the HOMO of **methyl 13** which was found to be composed primarily of the HBC HOMO containing significant contributions from both the ethyne (the lowest HOMO as an isolated molecule) and the Fe (Fig. 7).

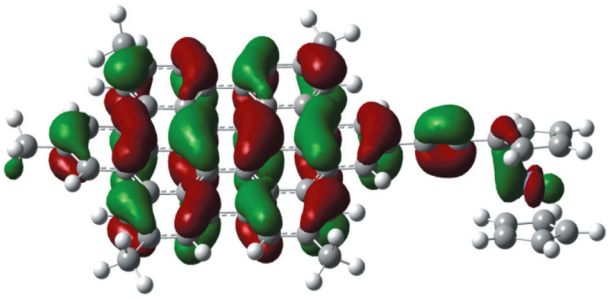

Fig. 7 HOMO of the methyl derivative of **13**, calculated at the MO6/6-31G(d,p) level.

While the HOMO provides information regarding the nature of the highest energy orbital, it does not provide information regarding the total charge redistribution. To assess this we performed Mullikan analysis (Table S1†) which shows that on going from ferrocene to ethynyl-ferrocene, the movement of charge occurs from the Fe and the ethynyl group to the attached cyclopentadienyl ring (Cp). (This is contrary to the commonly held view of ethynyl as electron withdrawing.) The addition of HBC increases the negative charge on the substituted cyclopentadiene and indeed on the acetylene linker itself which becomes integrated into an ethyne-HBC conjugated platform. The net effect is to depopulate the Fe further (and marginally depopulate the HBC).

The theoretical calculations show that the HOMO and LUMO states are not spatially different, indicating no charge transfer will occur upon excitation (assuming a primarily HOMO–LUMO transition). This is consistent with the experimental findings: *i.e.* no charge transfer in the ground state absorption spectra and an increase in the oxidation potential on going from ferrocene to **13**.

NLO properties of 13

A number of organic compounds have been studied as possible NLO materials as they offer some advantages over inorganic crystals. In general, organic NLO compounds comprise a bridged π-conjugation system and donor and acceptor end groups such as the fullerene–ferrocene dyads of Yamamoto *et al.*[34] (Scheme 3). One of these (**III**) is structurally related to **13**, and therefore **13** offered an interesting comparator to these results.

The nonlinear response of **13** was studied by hyper Rayleigh scattering (HRS)[35–37] at λ = 1.9 μm for comparison with those

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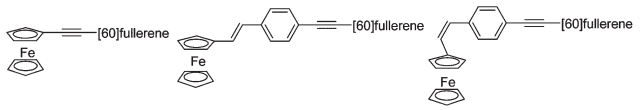

III *trans*-(**IV**) *cis*-(**IV**)

Scheme 3 Three fullerene–ferrocene dyads synthesised by Yamamoto *et al.*[34]

Table 3 NLO response for compound **13**, **III**, *trans*-(**IV**) and *cis*-(**IV**)

Complex	λ_0/νμ	$\beta^a/10^{-30}$ esu
13	396	260[a]
(**III**)	328	173[b]
trans-(**IV**)	329	568[b]
cis-(**IV**)	324	374[b]

[a] Measured in chloroform by the HRS method at 1.910 μm. [b] Measured in chloroform by the HRS method at 1.064 μm.

of (**III**), *trans*-(**IV**) and *cis*-(**IV**). As the UV-visible spectrum of **13** is complex, displaying several absorption bands, it was not appropriate to use a two-level dispersion model to infer a $\beta(0)$ that would be independent of the fundamental wavelength λ. From the data presented in Table 3 it is apparent that the β value for **13** (260×10^{-30} esu at λ = 1.91 μm) at a low resonance regime is higher than that of (**III**) (173×10^{-30} esu at λ = 1.06 μm) at a much more resonant regime. The direction and magnitude of this difference (a factor of 1.5) is particularly significant as all reported data on molecular NLO demonstrate an increase in β when the fundamental wavelength comes close to the absorption maxima (*i.e.* in a more resonant regime) even in rather complex spectra. The improvement in the β value also exceeds by far the experimental error of HRS measurements (10% in our case) and thus the increase in hyperpolarizability can be attributed to the greater electron-accepting character of the ethynyl-HBC relative to ethynyl-fullerene. Molecules with yet higher conjugation lengths such as that present in *trans*-(**IV**) serve to maximise the NLO response further and to suggest structural features that would constitute desirable additions to future synthetic targets.

Conclusions

A number of synthetically useful ferrocenyl substituted diketones, monoketones and acetylenes have been prepared as building blocks in the formation of polyphenylenes that comprise up to four ferrocenyl units. Oxidative cyclodehydrogenation *via* $FeCl_3$-catalysed oxidation was not successful; however hexa-*peri*-hexabenzocoronene (HBC) ethynyl ferrocene (**13**), a molecular form of organometallic graphene was prepared *via* Sonogashira coupling using iodo-HBC. The UV-visible absorption spectra, electrochemical and NLO data of this compound, confirm electron donation from the Fe to the highly delocalised Cp-ethynyl HBC unit. **13** is a novel conjugated organometallic graphene which warrants further solid-state investigation and synthetic derivatisation.

Experimental

Tetracyclone (Aldrich), ferrocene (Aldrich) and 3,-5-dimethoxybenzyl bromide **3** (Aldrich) were used as received. Ethynylferrocene[38] and dipyrimidyl acetylene[39] and the uncyclised iodo-polyphenylene precursor[20] were synthesised according to literature procedures. Flash chromatography was performed using silica gel (Brockman I, Aldrich Chemical) as the stationary phase. Preparative thin layer chromatography was performed using silica gel (1000 μm thickness) preparative thin layer chromatographic plates (Aldrich). NMR spectra were recorded in $CDCl_3$ using a Bruker Avance DPX-400 MHz spectrometer (operating at 400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C) or where stated using a Bruker AV-600 MHz spectrometer (600.1 MHz for ^{1}H, 150.6 MHz for ^{13}C). ^{1}H and ^{13}C NMR spectra were referenced relative to TMS (δ 0.00 ppm). Chemical shifts (δ) are reported in ppm and coupling constants in Hertz. IR spectra (reported in cm^{-1}) were made as neat samples and were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrometer equipped with a Universal-ATR sampling accessory. Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin. As is common for systems incorporating thermally robust polyaromatic frameworks, meaningful consistent elemental analysis results were difficult to obtain for compound **13** due to incomplete combustion of the fused all-carbon core. In the alternative, a ^{1}H NMR spectrum (Fig. 3) and the experimental (+)-MALDI-TOF spectra and $(MH)^+$ simulated isotopic distribution pattern for this compound (Supporting Information,† Fig. S1) are provided. Electrospray mass spectra were recorded on a Micromass-LCT spectrometer and accurate mass spectra were referenced against leucine enkephalin ($[M + H]^+$ *m/z* 556.2771 g mol^{-1}) and reported to within 5 ppm. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF premier spectrometer using an α-cyano-4-hydroxy cinnamic acid matrix and accurate mass spectra were referenced against [Glu^1]-fibrinopeptide B ($[M + H]^+$ *m/z* 1570.6768 g mol^{-1}) and reported to within 5 ppm. Cyclic voltammetry was performed using a CH Instruments Electrochemical Analyser Model 600B. Cyclic voltammograms were measured on 1 mM solutions using tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as supporting electrolyte. A standard three electrode cell was employed with a glassy carbon working electrode, a Pt wire counter electrode and a SCE as the reference electrode. Potentials are quoted *versus* the ferrocene–ferrocenium couple (0.0 V) and all potentials were referenced to internal ferrocene added at the end of each experiment. Solutions were degassed for several minutes by nitrogen bubbling before and during the experiment. UV-Vis absorption spectra were recorded as optically dilute solutions ($10^{-4} - 5 \times 10^{-7}$ M) in 1 × 1 cm^2 quartz cuvettes on a Shimadzu UV-2450 spectrophotometer.

Compound 1

Ferrocene (7.6 g, 40.8 mmol) was added to sulfuric acid (50 mL, spec. grav. 1.84) and the resulting deep blue ferrocenium solution was stirred at room temperature for 2 h. The solution was then poured into ice/water (200 mL) and allowed to warm to room temperature.

A solution of sodium nitrite (1.82 g, 13.2 mmol) in water (10 mL) at 0 °C was added dropwise to a stirred solution of

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4-aminobenzylalcohol (3.0 g, 24 mmol) in 1 : 1 water/hydrochloric acid (spec. grav. 1.18) (20 mL) at 0 °C, and stirred at this temperature for 30 min to ensure full diazotization. Copper powder (2.0 g) was added to the ferrocenium solution and the diazonium solution was added dropwise with vigorous stirring.

After 24 h stirring at room temperature, effervescence due to liberated nitrogen had ceased and ascorbic acid (10 g) was added to the dark mixture to reduce any remaining ferrocenium to ferrocene. Dichloromethane (200 mL) was added and the organic layer separated. The aqueous layer was extracted further with dichloromethane (4 × 100 mL), and the combined organic extracts were filtered through celite before removal of the solvent *in vacuo* to give a dark brown solid. This was subjected to column chromatography using gradient elution. The first yellow fraction, eluted with hexane, yielded ferrocene. The second orange-red fraction was eluted with dichloromethane and 5% methanol to give the desired product on removal of the solvents *in vacuo* as an orange solid (2.2 g, 31%). mpt: 109–110 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.50 (d, 2H, $^3J_{HH}$ = 8.3 Hz, –CH Ar), 7.31 (d, 2H, $^3J_{HH}$ = 8.3 Hz, –CH Ar), 4.69 (s, 2H, –C**H**$_2$–), 4.67 (t, 2H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.34 (t, 2H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.07 (s, 5H, –CH Fc), 1.73 (br s, 1H, –O**H**). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C): δ 138.34 (1C, quat Ar), 137.94 (1C, quat Ar), 126.78 (2C, –CH Ar), 125.82 (2C, –CH Ar), 84.60 (1C, quat Fc), 69.17 (5C, –CH Fc), 68.52 (2C, –CH Fc), 66.06 (2C, –CH Fc), 64.83 (1C, –**C**H$_2$). ESI-MS (toluene) for $C_{17}H_{16}FeO$: [M]$^+$ calculated *m*/*z* 292.0551, found *m*/*z* 292.0552. Anal. Calcd for $C_{17}H_{16}FeO{\cdot}CH_2Cl_2$: C, 57.33; H, 4.81. Found: C, 57.41; H, 4.87.

Compound 2

Compound **1** (1 g, 3.42 mmol) was dissolved in dichloromethane (20 mL) in a 3-necked round bottomed flask. The mixture was cooled to 0 °C, and a solution of phosphorous tribromide (0.7 mL, 1.85 g, 6.85 mmol) dissolved in dichloromethane (5 mL) was added dropwise. The resulting mixture was then stirred at 0 °C for 30 min. The reaction mixture was poured onto ice (100 g), neutralised with saturated aqueous sodium hydrogen carbonate solution and the organic phase separated. The aqueous phase was extracted with dichloromethane, and the organic phases were collected. These were washed with brine and dried over $MgSO_4$ to yield the product as an orange powder on the removal of the solvent *in vacuo* (1.14 g, 94%). mpt: >200 °C (decomp.). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.47 (d, 2H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 7.33 (d, 2H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 6.67 (t, 2H, $^3J_{HH}$ = 2.0Hz, –CH Fc), 4.54 (s, 2H, –C**H**$_2$–), 4.36 (s, 2H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.08 (s, 5H, –CH Fc). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C) δ: 139.46 (1C, quat Ar), 134.67 (1C, quat Ar), 128.69 (2C, –CH Ar), 125.97 (2C, –CH Ar), 84.13 (1C, quat Fc), 69.23 (5C, –CH Fc), 68.73 (2C, –CH Fc), 66.17 (2C, –CH Fc), 33.52 (1C, –**C**H$_2$). Anal. Calcd for $C_{17}H_{15}BrFe$: C, 57.51; H, 4.26. Found: C, 58.06; H, 4.42.

Compound 4

Calcium hydroxide (2.3 g, 31 mmol) and tetrabutylammonium hydrogensulfate (1.32 g, 3.88 mmol) were dissolved in 1 : 1 dichloromethane–water (180 mL). Argon was bubbled through the mixture for 30 min to degas the solution. Compound **2** (5.5 g, 15.5 mmol) and iron pentacarbonyl (1.1 mL, 7.75 mmol) were added to the reaction which was stirred at room temperature for six hours under a constant stream of argon. The reaction mixture was then oxidised in air and acidified with 10% HCl (120 mL). The aqueous phase was extracted with dichloromethane and the organic washings were combined and their volume reduced under vacuum. Column chromatography on silica yielded the product as an orange solid after the removal of solvent *in vacuo* (2.58 g, 58%). mpt: >200 °C (decomp.). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 7.45 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 7.11 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 4.65 (t, 4H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.34 (s, 4H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.07 (s, 10H, –CH Fc), 3.75 (s, 4H, –C**H**$_2$). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C): δ 205.47 (1C, –**C**O), 137.66 (2C, quat Ar), 131.02 (2C, quat Ar), 129.07 (4C, –CH Ar), 125.98 (4C, –CH Ar), 84.60 (2C, quat Fc), 69.18 (10C, –CH Fc), 68.49 (4C, –CH Fc), 66.05 (4C, –CH Fc), 48.41 (2C, –**C**H$_2$). ESI-MS (toluene) for $C_{35}H_{30}Fe_2ONa$: [M + Na]$^+$ calculated *m*/*z* 601.0893, found *m*/*z* 601.0919. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3092, 3031, ν(C═O st): 1722, ν(C═C st): 1612, 1603, 1527, ν(C–H rock Fc): 1103, 1083, 1056, 999. Anal. Calcd for $C_{35}H_{30}Fe_2O{\cdot}\frac{1}{2}H_2O$: C, 71.58; H, 5.32. Found: C, 71.82; H, 5.16.

Compound 5

Calcium hydroxide (3.2 g, 43.2 mmol) and tetrabutylammonium hydrogensulfate (1.83 g, 5.7 mmol) were dissolved in 1 : 1 dichloromethane–water (240 mL) and argon was bubbled through the reaction mixture for 30 min to degas the solution. 3,5-Dimethoxybenzyl bromide (**3**) (5.0 g, 21.6 mmol) was added followed by iron pentacarbonyl (1.5 mL, 10.8 mmol) and the reaction was stirred at room temperature for five and a half hours under a constant stream of argon. The reaction mixture was then oxidised in air and acidified with 10% HCl (120 mL). The aqueous phase was extracted with dichloromethane and the organic washings were combined and the volume reduced *in vacuo* to give a yellow/orange oil. The oil was subjected to column chromatography on silica. Eluting with diethyl ether yielded the desired product as an off-white waxy solid (2.3 g, 65%). mpt: 78–80 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 6.39 (t, 2H, $^4J_{HH}$ = 2.0 Hz, –CH Ar), 6.32 (d, 4H, $^4J_{HH}$ = 2.0Hz, –CH Ar), 3.78 (s, 12H, –OC**H**$_3$), 3.66 (s, 4H, –C**H**$_2$–). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C): δ 205.04 (1C, –**C**O), 160.51 (4C, quat Ar), 135.64 (2C, quat Ar), 107.07 (4C, –CH Ar), 98.71 (2C, –CH Ar), 54.86 (2C, –**C**H$_2$–), 48.78 (4C, –O**C**H$_3$). ESI-MS (methanol) for $C_{19}H_{22}O_5Na$: [M + Na]$^+$ calculated *m*/*z* 353.1365, found *m*/*z* 353.1374. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.34; H, 6.84.

Compound 6

4-Ferrocenylbenzoaldehyde (2 g, 6.89 mmol) and sodium cyanide (0.6 g, 12.2 mmol) were dissolved in water (3 mL) and ethanol (10 mL) and refluxed for 1 h. The solution was cooled, resulting in a red precipitate, which was collected by suction filtration. The precipitate was dried and subjected to column

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chromatography on silica eluting with dichloromethane. The first orange band yielded unreacted 4-ferrocenylbenzaldehyde and the second orange-red band afforded the desired product as an orange crystalline solid on recrystallisation from hexane (1.18 g, 59%). mpt: 117–118 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.87 (d, 2H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 7.47,(m, 4H, –CH Ar), 7.30 (d, 2H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 5.91 (d, 1H, $^3J_{HH}$ = 6.0 Hz, –C**H**(OH)), 4.68 (s, 2H, –CH Fc), 4.63 (s, 2H, –CH Fc), 4.55 (d, 1H, $^3J_{HH}$ = 6.0 Hz, –O**H**), 4.41 (s, 2H, –CH Fc), 4.32 (s, 2H, –CH Fc), 4.02 (s, 10H, –CH Fc). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C): δ 197.63 (1C, –**C**O), 146.39 (1C, quat Ar), 139.41 (1C, quat Ar), 136.52 (1C, quat Ar), 130.19 (1C, quat Ar), 128.84 (2C, –CH Ar), 127.30 (2C, –CH Ar), 126.19 (2C, –CH Ar), 125.31 (2C, –CH Ar), 83.95 (1C, quat Fc), 82.17 (1C, quat Fc), 75.25 (1C, –**C**H(OH)), 69.39 (5C, –CH Fc), 69.14 (5C, –CH Fc), 66.66 (2C, –CH Fc), 66.46 (2C, –CH Fc), 66.09 (2C, –CH Fc), 66.06 (2C, –CH Fc). ESI-MS (methanol) for $C_{34}H_{28}Fe_2O_2$: $[M]^+$ calculated *m*/*z* 580.0788, found *m*/*z* 580.0773. IR νbar (cm^{-1}): ν(O–H st): 3444, ν(C–H st, aromatic): 3095, 2960, ν(C═O st): 1665, ν(C═C st): 1601, 1561, 1526, ν(C–H rock Fc): 1106, 1069, 1031. Anal. Calcd for $C_{34}H_{28}Fe_2O_2$: C, 70.37; H, 4.86. Found: C, 70.42; H, 5.00.

Compound 7

(Reaction carried out in air.) Compound **6** (1.2 g, 2.07 mmol) was dissolved in chloroform (30 mL). Manganese dioxide (0.72 g, 8.27 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature, the solution was filtered through celite and the filtrant was washed until the filtrate ran clear. The solvent was removed *in vacuo* yielding the desired product as an orange-red solid (1.05 g, 88%). mpt: 134–135 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.93 (d, 4H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 7.57 (d, 4H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 4.77 (t, 4H, $^3J_{HH}$ = 1.5 Hz, –CH Fc), 4.47 (t, 4H, $^3J_{HH}$ = 1.5 Hz, –CH Fc), 4.07 (s, 10H, –CH Fc). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C): δ 193.71 (2C, –**C**O), 147.54 (2C, quat Ar), 129.95 (2C, quat Ar), 129.75 (4C, –CH Ar), 125.61 (4C, –CH Ar), 82.38 (2C, quat Fc), 70.14 (4C, –CH Fc), 69.78 (10C, –CH Fc), 66.89 (4C, –CH Fc). ESI-MS (methanol) for $C_{34}H_{26}Fe_2O_2Na$: $[MNa]^+$ calculated *m*/*z* 601.0529, found *m*/*z* 601.0532. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3096, 2961, ν(C═O, st): 1670, 1658, ν(C═C st): 1604, 1560, 1523, ν(C–H rock Fc): 1218, 1173, 1103, 1082. Anal. Calcd for $C_{34}H_{26}Fe_2O_2{\cdot}H_2O$: C, 68.49; H, 4.73. Found: C, 68.61; H, 4.73.

Compound 8

Diketone **7** (0.5 g, 0.86 mmol) and potassium hydroxide (0.08 g, 1.47 mmol) were dissolved in ethanol (25 mL) and heated to reflux. A solution of **4** (0.55 g, 0.95 mmol) dissolved in ethanol–dichloromethane, 1 : 1 (45 mL) and added dropwise to the mixture which was then refluxed for 18 h. The solution was cooled to room temperature, and the resulting precipitate was filtered and washed with ethanol followed by hexane to yield the desired product as an unstable purple solid (0.61 g, 63%). mpt: <100 °C (decomp.). ^{1}H NMR (600.1 MHz) ($CDCl_3$, 20 °C): δ 7.39 (d, 4H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 7.34 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 7.30 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.94 (d, 4H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 4.67 (t, 4H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.64 (t, 4H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.35 (t, 4H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.33 (t, 4H, $^3J_{HH}$ = 2.0 Hz, –CH Fc), 4.05 (s, 10H, –CH Fc), 4.04 (s, 10H, –CH Fc). ^{13}C {^{1}H} NMR (150.6 MHz) ($CDCl_3$, 20 °C): δ 200.74 (1C, –**C**O), 153.79 (2C, quat Ar), 139.94 (2C, quat Ar), 138.38 (2C, quat Ar), 130.76 (2C, quat Ar), 129.92 (4C, –CH Ar), 129.51 (4C, –CH Ar), 128.50 (2C, quat Ar), 125.53 (4C, –CH Ar), 124.95 (4C, –CH Ar), 124.49 (2C, quat Ar), 84.78 (2C, quat Fc), 83.70 (2C, quat Fc), 69.75 (10C, –CH Fc), 69.51 (10C, –CH Fc), 69.36 (4C, –CH Fc), 68.93 (4C, –CH Fc)), 66.32 (4C, –CH Fc), 66.25 (4C, –CH Fc). MALDI-TOF MS (methanol) for $C_{69}H_{52}Fe_4O$: $[M]^+$ calculated *m*/*z* 1120.1416, found *m*/*z* 1120.1416. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3076, ν(C═O st): 1706, ν(C═C st): 1600, 1526, 1517, ν(C–H rock Fc): 1103, 1088, 1082, 1017. Note: Instability of solid precluded C, H, N analysis.

Compound 9

Diketone **7** (1.3 g, 2.25 mmol) and potassium hydroxide (0.22 g, 3.85 mmol) were dissolved in ethanol (25 mL) and heated to reflux. A solution of **5** (0.79 g, 2.4 mmol) was dissolved in ethanol (25 mL) and added dropwise to the reaction mixture which was refluxed for 3 h. The solution was then cooled slowly to room temperature and the dark green crystalline product was isolated by filtration (0.38 g, 64%). mpt: 204–205 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.32 (d, 4H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 6.91 (d, 4H, $^3J_{HH}$ = 8.5 Hz, –CH Ar), 6.51 (d, 4H, $^4J_{HH}$ = 2.0 Hz, –CH Ar), 6.39 (t, 2H, $^4J_{HH}$ = 2.0 Hz, –CH Ar), 4.64 (t, 4H, $^3J_{HH}$ = 1.8 Hz, –CH Fc), 4.34 (t, 4H, $^3J_{HH}$ = 1.8 Hz, –CH Fc), 4.01 (s, 10H, –CH Fc), 3.66 (s, 12H, –OC**H**$_3$). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C) δ: 199.36 (1C, –**C**O), 159.81 (4C, quat Ar), 154.30 (2C, quat Ar), 139.78 (2C, quat Ar), 132.17 (2C, quat Ar), 129.98 (2C, quat Ar), 129.16 (4C, –CH Ar), 124.68 (4C, –CH Ar), 124.26 (2C, quat Ar), 107.47 (4C, –CH Ar), 100.11 (2C, –CH Ar), 83.40 (2C, quat Fc), 69.37 (10C, –CH Fc), 69.04 (4C, –CH Fc), 65.96 (4C, –CH Fc), 54.71 (4C, –O**C**H$_3$). ESI-MS (toluene) for $C_{53}H_{44}Fe_2O_5$: $[M]^+$ calculated *m*/*z* 872.1888, found *m*/*z* 872.1897. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3086, 2997, ν(C–H st, –OCH$_3$): 2834, ν(C═O st): 1702, ν(C═C st): 1603, 1589, 1524, ν(C–O st, –OCH$_3$): 1275, ν(C–H rock Fc): 1193, 1104, 1096, 1044. Anal. Calcd for $C_{53}H_{44}Fe_2O_5$: C, 72.95; H, 5.08. Found: C, 72.71; H, 4.89.

Compound 10

Cyclopentadienone **8** (0.25 g, 0.22 mmol), di(5-pyrimidyl)acetylene (0.037 g, 0.2 mmol) and benzophenone (1.0 g) were mixed in a round bottomed flask and attached to an air condenser. The mixture was heated at 200 °C for 18 h. The mixture was then subjected to flash column chromatography on silica. Eluting with dichloromethane removed all the benzophenone and any un-reacted cyclopentadienone. Elution with diethyl ether–methanol (10 : 1) and removal of the solvents yielded the desired product as a light orange powder (0.14 g, 54%). mpt: >200 °C (decomp.). ^{1}H NMR (600.1 MHz) ($CDCl_3$, 20 °C): δ 8.81 (s,

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2H, –CH Ar), 8.32 (s, 4H, –CH Ar), 7.12 (d, 4H, $^3J_{H1H}$ = 8.0 Hz, –CH Ar), 7.07 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.81 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.78 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 4.53 (s, 4H, –CH Fc), 4.48 (s, 4H, –CH Fc), 4.26 (s, 4H, –CH Fc), 4.21 (s, 4H, –CH Fc), 3.92 (s, 10H, –CH Fc), 3.91 (s, 10H, –CH Fc). ^{13}C {^{1}H} NMR (150.6 MHz) ($CDCl_3$, 20 °C) δ: 157.98 (4C, –CH Ar), 156.05 (2C, –CH Ar), 142.42 (2C, quat Ar), 141.48 (2C, quat Ar), 137.48 (2C, quat Ar), 136.85 (2C, quat Ar), 136.68 (2C, quat Ar), 136.04 (2C, quat Ar), 133.90 (2C, quat Ar), 133.06 (2C, quat Ar), 131.18 (4C, –CH Ar), 131.08 (4C, –CH Ar), 124.68 (4C, –CH Ar), 124.21 (4C, –CH Ar), 84.23 (2C, quat Fc), 83.61 (2C, quat Fc), 69.74 (10C, –CH Fc), 69.69 (10C, –CH Fc), 69.00 (4C, –CH Fc), 66.12 (4C, –CH Fc), 66.02 (4C, –CH Fc), 60.05 (4C, –CH Fc). MALDI-TOF MS for $C_{78}H_{58}Fe_4N_4$: $[M]^+$ calculated *m*/*z* 1274.2059, found *m*/*z* 1274.2003. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3093, 3024, ν(C═C st): 1608, ν(C═N st): 1548, 1529, ν(C–H rock Fc): 1104, 1082, 1049, 1019. Anal. Calcd for $C_{78}H_{58}Fe_4N_4{\cdot}\frac{1}{2}CH_3OH$: C, 73.20; H, 4.65; N, 4.36. Found: C, 73.17; H, 4.67; N, 4.40.

Compound 11

Cyclopentadienone **9** (0.4 g, 0.46 mmol), dipyrimidyl acetylene (0.075 g, 0.41 mmol) and benzophenone (1.5 g) were mixed in a round bottomed flask and attached to an air condenser. The mixture was heated at 200 °C for 18 h. The mixture was then subjected to flash column chromatography on silica. Eluting with dichloromethane removed all the benzophenone and any un-reacted cyclopentadienone. Elution with diethyl ether–methanol (9 : 1) and removal of the solvents *in vacuo* yielded the desired product as an orange powder (0.24 g, 58%). mpt: >200 °C (decomp.). ^{1}H NMR ($CDCl_3$, 20 °C): δ 8.86 (s, 2H, –CH Ar), 8.33 (s, 4H, –CH Ar), 7.05 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.80 (d, 4H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.05 (m, 6H, –CH Ar), 4.55 (s, 4H, –CH Fc), 4.26 (s, 4H, –CH Fc), 3.89 (s, 10H, –CH Fc), 3.52 (s, 12H, –OC**H**$_3$). ^{13}C {^{1}H} NMR (600 MHz) ($CDCl_3$, 20 °C): δ 159.87 (4C, quat Ar), 157.68 (4C, –CH Ar), 156.09 (2C, quat Ar), 142.40 (2C, quat Ar), 141.34 (2C, quat Ar), 140.21 (2C, quat Ar), 136.77 (2C, quat Ar), 136.68 (2C, quat Ar), 133.73 (2C, quat Ar), 132.62 (2C, –CH Ar), 130.57 (4C, –CH Ar), 124.15 (4C, –CH Ar), 109.85 (4C, –CH Ar), 98.51 (2C, –CH Ar), 84.36 (2C, quat Fc), 69.81 (10C, –CH Fc), 69.12 (4C, –CH Fc), 66.05 (4C, –CH Fc), 55.03 (4C, –O**C**H$_3$). MALDI-TOF MS; for $C_{62}H_{50}Fe_2N_4O_4$: $[M]^+$ calculated *m*/*z* 1026.2531, found *m*/*z* 1026.2560. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3024, 2939, ν(C–H st, –OCH$_3$): 2837, ν(C═C st): 1607, ν(C═N st): 1603, 1550, ν(C–O st, –OCH$_3$): 1279, ν(C–H rock Fc): 1200, 1161, 1136. Anal. Calcd for $C_{62}H_{50}Fe_2N_4O_4$: C, 72.52; H, 4.91; N, 5.46. Found: C, 72.70; H, 4.71; N, 5.24.

Compound 12

1,2-Bis(*p*-ferrocenylphenyl)acetylene (0.15 g, 0.27 mmol), **9** (0.30 g, 0.34 mmol) and benzophenone (2 g) were mixed in a round bottomed flask and attached to an air condenser. The mixture was heated at 190 °C for 24 h. The mixture was then subjected to flash column chromatography on silica. Eluting with dichloromethane followed by recrystallisation from hexane yielded the desired product as an orange-red powder (0.07 g, 18%). mpt: >200 °C (decomp.). ^{1}H NMR ($C_2D_2Cl_4$, 60 °C): δ 7.06 (d, 8H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.83 (d, 8H, $^3J_{HH}$ = 8.0 Hz, –CH Ar), 6.14 (d, 4H, $^4J_{HH}$ = 2.0 Hz, –CH Ar), 6.02 (t, 2H, $^4J_{HH}$ = 2.0 Hz, –CH Ar), 4.54 (s, 8H, –CH Fc), 4.23 (s, 8H, –CH Fc), 3.91 (s, 20H, –CH Fc), 3.48 (s, 12H, –OC**H**$_3$). ^{13}C {^{1}H} NMR (150.6 MHz) ($CDCl_3$, 20 °C) δ: 159.23 (4C, quat Ar), 142.42 (2C, quat Ar), 140.13 (2C, quat Ar), 139.91 (4C, quat Ar), 138.44 (2C, quat Ar), 136.06 (4C, quat Ar), 130.97 (8C, –CH Ar), 123.89 (8C, –CH Ar), 110.09 (4C, –CH Ar), 97.57 (2C, –CH Ar), 70.17 (8C, –CH Fc), 69.30 (4C, quat Fc), 66.19 (8C, –CH Fc), 54.87 (24C, –CH Fc & –O**C**H$_3$). MALDI-TOF MS for $C_{86}H_{70}Fe_4O_4$: $[M]^+$ calculated *m*/*z* 1390.2672, found *m*/*z* 1390.2739. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3088, 3020, ν(C–H st, –OCH$_3$): 2952, 2833, ν(C═C st): 1606, 1562, 1529, ν(C–O st, –OCH$_3$): 1274, ν(C–H rock Fc): 1158, 1104, 1062. Anal. Calcd for $C_{86}H_{70}Fe_4O_4$: C, 74.27; H, 5.07. Found: C, 74.04; H, 4.83.

Iodo-HBC

A solution of iron(III) chloride (1.8 g, 14.0 mmol) in nitromethane (3 mL) was added dropwise to a stirred solution of the uncyclised iodo-polyphenylene precursor (0.35 g, 0.47 mmol) in dichloromethane (40 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for 45 min the reaction was quenched with methanol (40 mL). The precipitate was filtered, washed with methanol (100 mL) and dried under reduced pressure. The crude product was purified by column chromatography on silica, elution with hexane–dichloromethane (4 : 1) and removal of the solvents yielded the desired product as an off-white crystalline solid (0.30 g, 85%). mpt: >300 °C. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 9.20 (s, 2H, –CH Ar), 9.15 (s, 2H, –CH Ar), 9.07 (s, 2H, –CH Ar), 8.96 (s, 2H, –CH Ar), 8.86 (s, 2H, –CH Ar), 8.69 (s, 2H, –CH Ar), 1.95 (s, 9H, –C(C**H**$_3$)$_3$), 1.91 (s, 18H, –C(C**H**$_3$)$_3$), 1.82 (s, 18H, –C(C**H**$_3$)$_3$). ^{13}C {^{1}H} NMR ($CDCl_3$, 20 °C): δ 148.56 (quat Ar), 148.40 (quat Ar), 148.37 (quat Ar), 131.97 (quat Ar), 130.17 (quat Ar), 129.92 (quat Ar), 129.84 (quat Ar), 129.68 (quat Ar), 129.61 (2C, –CH Ar), 128.23 (quat Ar), 124.06 (quat Ar), 123.25 (quat Ar), 123.21 (quat Ar), 123.09 (quat Ar), 120.22 (quat Ar), 119.83 (quat Ar), 119.72 (quat Ar), 118.95 (quat Ar), 118.88 (2C, –CH Ar), 118.85 (2C, –CH Ar), 118.58 (2C, –CH Ar), 118.54 (2C, –CH Ar), 118.48 (2C, –CH Ar), 35.65 (1C, quat –**C**(CH$_3$)$_3$), 35.59 (2C, quat –**C**(CH$_3$)$_3$), 35.52 (2C, quat –**C**(CH$_3$)$_3$), 32.01 (3C, –CH, –C(**C**H$_3$)$_3$), 31.98 (6C, –CH, –C(**C**H$_3$)$_3$), 31.93 (6C, –CH, –C(**C**H$_3$)$_3$). MALDI-TOF MS calculated for $C_{62}H_{57}I$: $[M]^+$ calculated *m*/*z* 928.3505, found *m*/*z* 928.3549. IR νbar (cm^{-1}): ν(C–H st, aromatic): 3099, ν(C–H st, –CH$_3$): 2953, 2902, 2866. Anal. Calcd for $C_{62}H_{57}I$: C, 80.16; H, 6.18. Found: C, 79.92; H, 6.03.

Compound 13

Ethynylferrocene (0.027 g, 0.13 mmol) was dissolved in triethylamine (3 mL) and added *via* cannula to a solution of iodo-HBC (0.1 g, 0.11 mmol) and tetrakis(triphenylphosphino)palladium

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(0.006 g, 0.006 mmol) in toluene (8 mL). The mixture was heated at 70 °C for 18 h. The solvents were removed *in vacuo*, washed with water and extracted into dichloromethane. The organic phase was dried over $MgSO_4$, solvents removed *in vacuo* again before being subjected to column chromatography on silica. Elution with hexane–dichloromethane (1 : 1) followed by recrystallisation from methanol yielded the desired product as a fine orange-red powder (0.08 g, 77%). mpt: >200 °C (decomp.). ^{1}H NMR (600.1 MHz) ($CDCl_3$, 20 °C): δ 9.24 (s, 2H, –CH Ar), 9.18 (s, 2H, –CH Ar), 9.13 (s, 2H, –CH Ar), 9.04 (s, 2H, –CH Ar), 8.91 (s, 2H, –CH Ar), 8.81 (s, 2H, –CH Ar), 4.85 (s, 2H, –CH Fc), 4.50 (s, 5H, –CH Fc), 4.46 (s, 2H, –CH Fc), 1.98 (s, 9H, –C(C**H**$_3$)$_3$), 1.95 (s, 18H, –C(C**H**$_3$)$_3$), 1.89 (s, 18H, –C(C**H**$_3$)$_3$). ^{13}C {^{1}H} NMR (150.6 MHz) ($CDCl_3$, 20 °C): δ 148.72 (quat Ar), 148.69 (quat Ar), 148.61 (quat Ar), 130.49 (quat Ar), 130.31 (quat Ar), 130.14 (quat Ar), 130.10 (quat Ar), 129.98 (quat Ar), 129.28 (quat Ar), 124.80 (quat Ar), 124.21 (2C, –CH Ar), 123.52 (quat Ar), 123.49 (quat Ar), 123.47 (quat Ar), 121.46 (quat Ar), 120.47 (quat Ar), 120.30 (quat Ar), 120.12 (quat Ar), 119.59 (quat Ar), 119.32 (2C, –CH Ar), 118.99 (2C, –CH Ar), 118.83 (2C, –CH Ar), 118.80 (2C, –CH Ar), 118.78 (2C, –CH Ar), 91.50 (1C, quat Fc), 89.21 (1C, –C≡C–), 87.39 (1C, –C≡C–), 71.51 (2C, –CH Fc), 69.98 (5C, –CH Fc), 68.93 (2C, –CH Fc), 35.62 (3C, quat, –**C**(CH$_3$)$_3$), 35.59 (2C, quat, –**C**(CH$_3$)$_3$), 31.98 (6C, –CH, –C(**C**H$_3$)$_3$), 31.94 (9C, –CH, –C(**C**H$_3$)$_3$). MALDI-TOF MS for $C_{74}H_{66}Fe$: $[M]^+$ calculated *m*/*z* 1010.4514, found *m*/*z* 1010.4509. IR ν (cm^{-1}): ν(C–H st, aromatic): 3099, ν(C–H st, –CH$_3$): 2954, 2904, 2666, ν(C≡C st): 2200 ν(C=C st): 1606, 1578, ν(C–H rock Fc): 1090, 1055.

NLO measurements

The harmonic light scattering (HLS) technique involves the detection of the incoherently scattered second harmonic generated by a solution of the molecule under irradiation with a laser of wavelength λ, leading to the measurement of the mean value of the $\beta \times \beta$ tensor product, $<\beta_{HLS}>$. The square root of this value is quoted as β. In the present work, β measurements have been made using λ = 1.91 μm as the fundamental wavelength. As the harmonic wavelength at 955 nm is far away from the 2-photon resonance, any contribution from 2-photon fluorescence to the HLS signal is negligible. The 1.91 μm fundamental beam is emitted by a high-pressure hydrogen (30 bars) Raman cell (l = 50 cm), pumped by a Nd^{3+} : YAG laser operating at 1.06 μm and providing a 10 Hz repetition rate with 15 ns duration pulses.

Our reference sample is a concentrated (5×10^{-3} mol L^{-1}) solution of Crystal Violet. Its octupolar β value is 170×10^{-30} esu at 1.91 μm. It must be noted that most classical organic solvents are not transparent at 1.9 μm. Chloroform is the most suitable standard solvent in this wavelength range. It can be used in a fluorescence cell (l = 1 cm) in order to minimise propagation losses over the typical 0.5 cm actual interaction length within the solution. HRS photons emitted at 955 nm are collected at a 90° angle with respect to the direction of the incident beam, and are focused onto a PMT using two collecting lenses. The detected signal is then sampled and averaged using a Boxcar and processed by a computer. The reference beam is collected at a 45° incidence angle by a glass plate and focused onto a highly nonlinear NPP (N-4-nitrophenyl-prolinol) powder used as a frequency doubler. The variation of the scattered second harmonic intensity from the solution is recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder. β values are then inferred from the slopes of the resulting lines. The relative experimental error for β values is ≤10%.

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