Synthesis of supramolecular fullerene–porphyrin–Cu(phen)$_2$–ferrocene architectures. A heteroleptic approach towards tetrads†

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Received 28th September 2006, Accepted 25th October 2006
First published as an Advance Article on the web 16th November 2006
DOI: 10.1039/b614111k

Four supramolecular fullerene–porphyrin–Cu(phen)$_2$–ferrocene architectures were accessed by a twofold coordination strategy. At first, the phenanthroline-linked zinc porphyrins **1–4**, conceived as supramolecular synthons, were combined with a ferrocene module, 3,8-(diferrocenylethynyl)-phenanthroline (**5**), by a Cu(I)-mediated heteroleptic bisphenanthroline complexation (HETPHEN) protocol to furnish the porphyrin–Cu(phen)$_2$–ferrocene aggregates **6–9**. Subsequently, the fullerene module **10** was incorporated by axial pyridyl coordination to the zinc porphyrin, affording **11–14**. Their suitability as tetrads was interrogated using electrochemical and photophysical data.

Introduction

The conversion of solar into chemical energy is probably the most important and consequential step occurring in the photosynthetic reaction centre in plants.[1] In purple photosynthetic bacteria for instance, efficient light harvesting and excitation energy transfer (EET) funnels solar energy from the photosystems LH2 and LH1 to the special pair bacteriochlorophyll dimer (Bchl$_2$).[1] The subsequent cascade of very fast electron transfer (eT) steps produces a charge-separated (CS) state Bchl$_2^{\bullet+}$ Q$_a^{\bullet-}$ (quinone) over a fairly large distance.[2] Charge recombination (CR) is effectively avoided until the hole and electron are separated by a membrane.

Major efforts have been made in past decades towards mimicking this process and in developing artificial photosynthetic systems.[3,4] An important class of compounds showing long-lived CS states are the fullerene-porphyrin-ferrocene triads, tetrads and pentads.[5] In particular, highly efficient photosynthetic electron transfer has been realised by Fukuzumi, Guldi, Imahori, Ito and colleagues[6] in ferrocene–zinc porphyrin–C$_{60}$ triads, in which the relatively long-lived CS state (up to 16 μs) could be produced with an extremely high quantum yield (nearly unity). They also reported a ferrocene–zinc porphyrin trimer–fullerene pentad,[7] which exhibited not only the longest lifetime (0.53 s in PhCN at 163 K) of a CS state, but also an extremely high CS efficiency (83%), comparable to the eT properties of bacteriochlorophyll dimer radical cation (Bchl$_2^{\bullet+}$)–secondary quinone radical anion (Q$_B^{\bullet-}$) ion pair in the bacterial photosynthetic reaction centre.

However, while in the natural photosynthetic reaction centre the eT process occurs along a supramolecular relay system in a protein matrix, most of the above-mentioned reports represent covalent systems. Construction of well defined structures bearing three or more different functional photo/redox active units is tedious in a dynamic supramolecular regime.[4a,d,8] It is hence not surprising that very few reports of supramolecular triads,[9] and none of tetrads, are known. Invariably, in the fullerene–porphyrin–ferrocene triads known so far[9] there is only one non-covalent binding motif present, and either the fullerene or the ferrocene is covalently bound to the porphyrin. A supramolecular triad/tetrad where both the ferrocene and the fullerene subunits are bound solely by non-covalent interactions has been difficult to access. In the present study, we demonstrate how a combination of two orthogonal binding modes – involving (i) Cu(I)-mediated heteroleptic bisphenanthroline complexation and (ii) axial binding of pyridine to zinc porphyrin – is used effectively to obtain four supramolecular fullerene–porphyrin–Cu(phen)$_2$–ferrocene aggregates, as a proof of principle for the heteroleptic construction of tetrads. The Cu(phen)$_2$ complex, apart from playing a structural role as a non-covalent binding unit, is known to efficiently mediate electron transfer between Zn(II) and Au(III) porphyrins, as reported by Sauvage,[10] and is also known to be involved in photoinduced eT processes with the C$_{60}$ moiety.[11]

Results and discussion

The strategy to the supramolecular aggregates involves three steps: (i) synthesis of phenanthroline-linked porphyrins **1–4**; (ii) Cu(I)-driven heteroleptic bis-phenanthroline complexation of **1–4** with bis(ferrocenylethynyl)phenanthroline **5** to afford the Cu(I)-mediated supramolecular porphyrin–Cu(phen)$_2$–ferrocene aggregates **6–9**; and (iii) axial coordination of pyridyl fullerene **10** to **6–9** to furnish the supramolecular fullerene–porphyrin–ferrocene systems **11–14**.

Synthesis of phenanthroline-appended porphyrins 1–4

Our strategy towards the synthesis of **1–4** was to attach phenanthroline[12] **Phen1** to the iodophenyl groups in porphyrins **P1–P4** *via* a Sonogashira cross-coupling. Compounds **1** and **4** have already been reported by us elsewhere.[13]

In order to access the required phenanthroline–porphyrin hybrids **1–4**, the *meso*-iodophenyl zinc-porphyrins **P1–P4** were first synthesised based on strategies outlined by Lindsey *et al.*[14] A subsequent Sonogashira reaction using Pd$_2$(dba)$_3$/AsPPh$_3$ in

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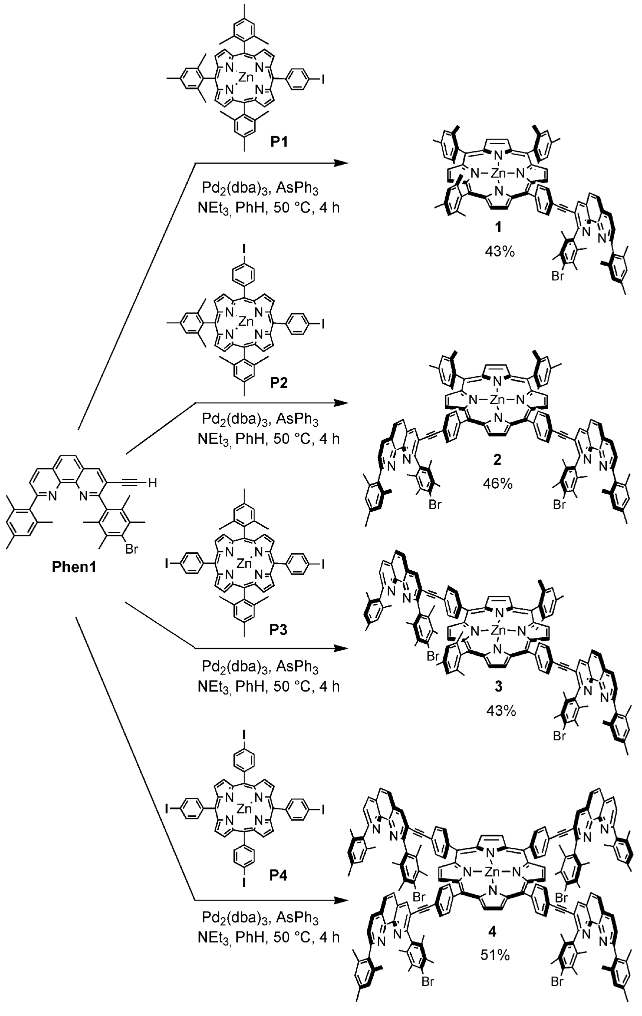
† Electronic supplementary information (ESI) available: Fig. S1–S27, Tables S1–S3, and crystal structure data for **5**. See DOI: 10.1039/b614111k

benzene or pyridine with triethylamine as a base allowed for the cross-coupling between **Phen1** and **P1–P4**, to furnish **1–4** (Scheme 1). Purification of **1–4** was realised by chromatography on silica-gel followed by size-exclusion chromatography on bio-beads in toluene.



Scheme 1 Synthesis of phenanthroline–porphyrin hybrids **1–4**.

Table S1 (see ESI†) displays the various NMR shifts of **1–4** measured in CD_2Cl_2. It was noticed that the H_β protons of the pyrrole units of the porphyrin rings were split according to the symmetry of the ligands. The distinct attachment in the *meso* position of the porphyrin did, however, not entail tangible NMR shift differences of the phenanthroline protons. The sole difference noted was an upfield shift for the 4,7- and 5,6-protons on the phenanthroline unit of **4**, compared to their counterparts in **1**, **2**, and **3**.

Absorption spectroscopy (Table 1) showed an increasing bathochromic shift of the Soret band from **1** to **4** relative to zinc 5,10,15,20-tetraphenylporphyrin (**ZnTPP**), *i.e.* with the growing number of phenanthrolines at the periphery of the zinc porphyrin core (Fig. 1). Also noticed was the predicted increase in the absorption coefficient of the phenanthroline chromophore in **1–4** in the 250–350 nm region. The ligands displayed strong fluorescence when excited at the Soret band.

Table 1 Absorption and emission maxima of **1–4**

	$\lambda_{abs}{}^a$/nm	$\lambda_{em}{}^b$/nm
1	289, 421*, 512, 549, 588	599, 648
2	289, 424*, 550, 590	600, 648
3	289, 424*, 550, 591	602, 653
4	289, 428*, 551, 590	606, 652

[a] Measured in CH_2Cl_2. [b] Excited at the Soret (*) absorption maximum.

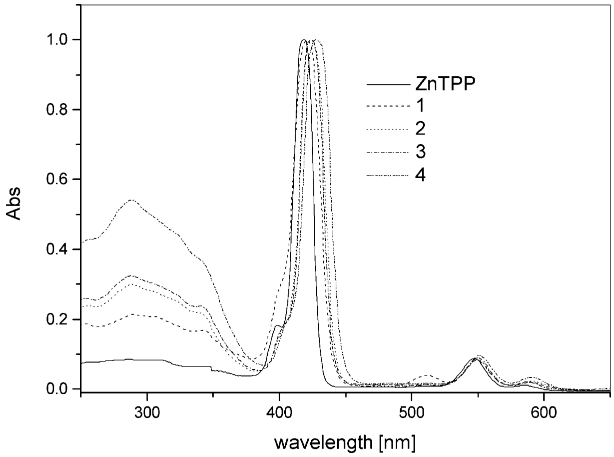


Fig. 1 Absorption spectra of **1–4** measured in CH_2Cl_2 normalised at the Soret band.

Formation of porphyrin–Cu(phen)$_2$–ferrocene aggregates by the HETPHEN complexation strategy

Ligands **1–4** are supramolecular building blocks, which can be utilised for the construction of porphyrin–Cu(phen)$_2$–ferrocene systems by a metal-driven heteroleptic complexation. As a proof of concept, we have recently incorporated phenanthrolinyl porphyrin **1** into a multicomponent self-assembled stack.[13b] Along the same lines, the tetrakis(bis-heteroleptic) supramolecular phenanthroline complex **9** was realised starting from porphyrin **4** through a Cu(I)-mediated approach.[13a] Accordingly, the supramolecular aggregates **6–8** (Chart 1) were prepared based on the HETPHEN[15] approach. For this purpose, compound **5** was synthesised by a Sonogashira reaction of ferrocenylacetylene with 3,8-dibromophenanthroline using $[Pd(PPh_3)_2]Cl_2$/CuI and NH^iPr_2 (Scheme 2). Single crystals of **5** were obtained by slow diffusion of hexane into a concentrated solution of **5** in chloroform. Fig. 2 displays the crystal structure of **5**.

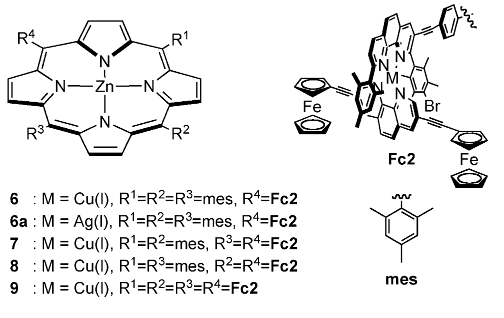
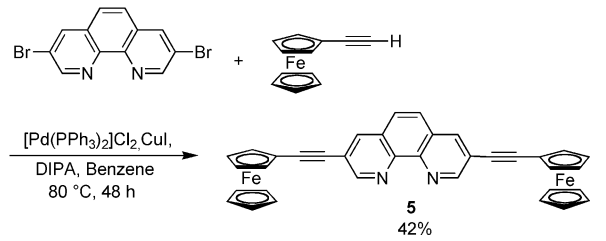


Chart 1 Chemical representation of triads **6–9** and **6a**.



Scheme 2 Synthesis of diferrocenylethynylphenanthroline **5**.

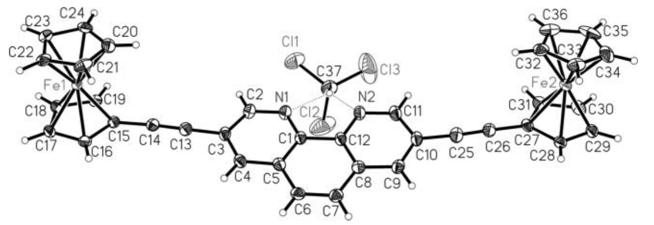


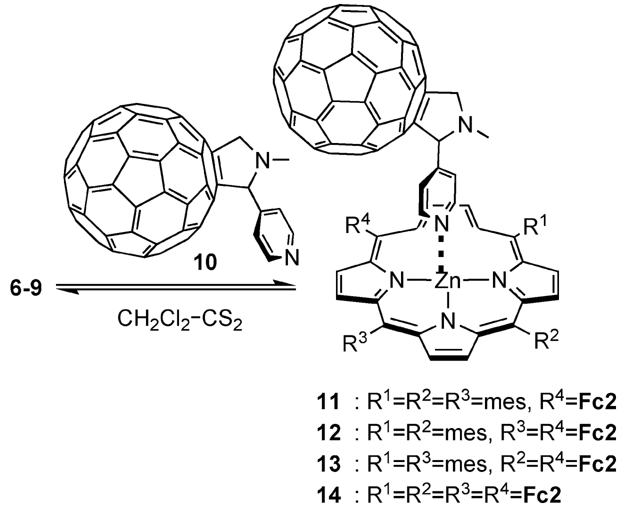
Fig. 2 Crystal structure of **5** (the non-H atoms are shown with 50% probability ellipsoids).

X-Ray structure of 5‡. In the crystal structure of **5**, the phenanthroline unit showed a small distortion from planarity with a mean deviation of the non-H atoms from the best plane of 0.048 Å. Both ferrocenyl groups were found in approximately eclipsed conformations. The angle between the best plane of the phenanthroline group and the plane through C15–C17–C19 was found to be 13.4°. Similarly, the angle between the best plane of the phenanthroline group and the plane through C27–C29–C31 was 14.8°. The crystal structure revealed a chloroform solvate being hydrogen-bonded to the two N atoms of the phenanthroline group. The phenanthroline units formed stacks along the *b*-direction (see ESI†). Neighbouring phenanthrolines in the stacks showed partial overlapping π-systems in the region C6–C7–C8–C9–C10–C11, with shortest interatomic π–π distances being 3.27 and 3.35 Å. In addition, the structure also indicated two intermolecular C(ferrocenyl)–H–π(ferrocenyl) contacts and a short intermolecular C(ferrocenyl)H–Cl interaction.

HETPHEN complexation[15]. Heteroleptic complexation of **1–4** with **5**, furnishing complexes **6–9** in quantitative yield, was effected using $[Cu(CH_3CN)_4]PF_6$ in dichloromethane. The formation of **6–9** was clearly ascertained by observation of the molecular ion peaks in the ESI-MS and by diagnostic NMR upfield shifts of the 3″,5″-protons of the mesityl groups of the phenanthroline units (see ESI†).

Formation of supramolecular fullerene–porphyrin–Cu(phen)$_2$–ferrocene systems

Reaction of **6–9** with **10** in CH_2Cl_2–CS_2 (1 : 1) afforded **11–14** (Scheme 3, Chart 2). Their formation was readily detected by UV-vis spectroscopy, because the Soret band of **11–14** displayed a characteristic bathochromic shift from 420 nm to 430 nm. In addition, characteristic shifts of various signals in the ^{1}H NMR were noticed. Notably, the H_β pyrrole signals of the porphyrin were found to shift by ~0.1 ppm upfield in all complexes. The signal for the 3″,5″-mesitylene protons ($C_6H_2Me_3$) experienced a downfield shift from δ 6.14 in **6–9** to δ 6.21 in **11–14**. (Table S2†). Likewise, the signals corresponding to the ferrocene protons were found shifted upfield by ~0.1 ppm. This could arise due to the proximity of the ferrocene to the fullerene subunit.



11 : R^1=R^2=R^3=mes, R^4=**Fc2**
12 : R^1=R^2=mes, R^3=R^4=**Fc2**
13 : R^1=R^3=mes, R^2=R^4=**Fc2**
14 : R^1=R^2=R^3=R^4=**Fc2**

Scheme 3 Reaction leading to formation of **11–14**.

The ^{1}H NMR spectra of **6** and **11** are shown in Fig. 3. A distinct upfield shift of the 3,5-pyridyl protons of **10** from δ 7.76 ppm (as free residue) to a broad singlet at δ 6.44 (in **11**) was noticed. The signals of the protons from the pyrrolidine ring fused to C_{60}, at δ 4.67 and 3.92, also experienced an upfield shift from δ 5.02 and 4.32 in **10**. Similar shifts were found in **12**, **13** and **14**. Due to the density of methyl signals, the 2,6-pyridyl protons, known to shift drastically upfield to the region δ 0.5–2.0, were not readily discernible.

The sharp signals in the NMR spectra suggest that there is free rotation about the various axes present in **11–14**. In addition, no broadening of any signals in **11–14** was observed compared to **6–9**. Presence of a single set of ferrocene signals was noticed in **11**, **12** and **14**, implying equal interaction of the fullerene with all the ferrocene protons.

ESI-MS characterisation[16] revealed molecular ion signals for **11–14**, not unexpectedly accompanied by signals from **6–9**. Within the range of the instrument, isotopic splitting patterns were obtained for **12–14**, matching with those of the simulated spectra.

UV-Visible absorption titrations of **6–9** with **10** in dichloroethane at 298 K exhibited spectral changes characteristic of axial coordination of a pyridine ligand to a zinc porphyrin.[17] The formation constants *K* for the porphyrin–fullerene conjugates could be determined from the spectral data by SPECFIT.[18] The association constants are listed in Table 2. Notably, the association

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‡ Crystal structure: a single crystal (a brown blade with dimensions 0.04 × 0.26 × 0.75 mm) was measured on a SIEMENS SMART 1 K CCD diffractometer with Mo-Kα radiation at a temperature of about 158 K. Repeatedly measured reflections remained stable. An empirical absorption correction with program SADABS[22] gave a correction factor between 0.804 and 0.952. 49 615 reflections measured, 9002 unique reflections, $R(I)_{int} = 0.063$. The structure was determined by direct methods and refined by least-squares against all measured F^2 values.[23] The H atoms were positioned geometrically and were constrained. $C_{36}H_{24}Fe_2N_2{\cdot}CHCl_3$, $M = 715.64$, monoclinic, space group $P2_1/c$ (no. 14), $a = 22.770(3)$, $b = 7.5283(11)$, $c = 19.570(3)$ Å, $\beta = 111.923(12)°$, $V = 3112.1(8)$ Å^3, $Z = 4$, $D_x = 1.527$ g cm^{-3}, $\mu = 1.22$ mm^{-1}, 397 refined parameters, $R_1(F)[I > 2\sigma(I)] = 0.052$, GOOF = 1.02, the final difference density was between −1.12 and +1.07 e Å^{-3} near Cl atoms of the chloroform solvate group. CCDC reference number 622456. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614111k

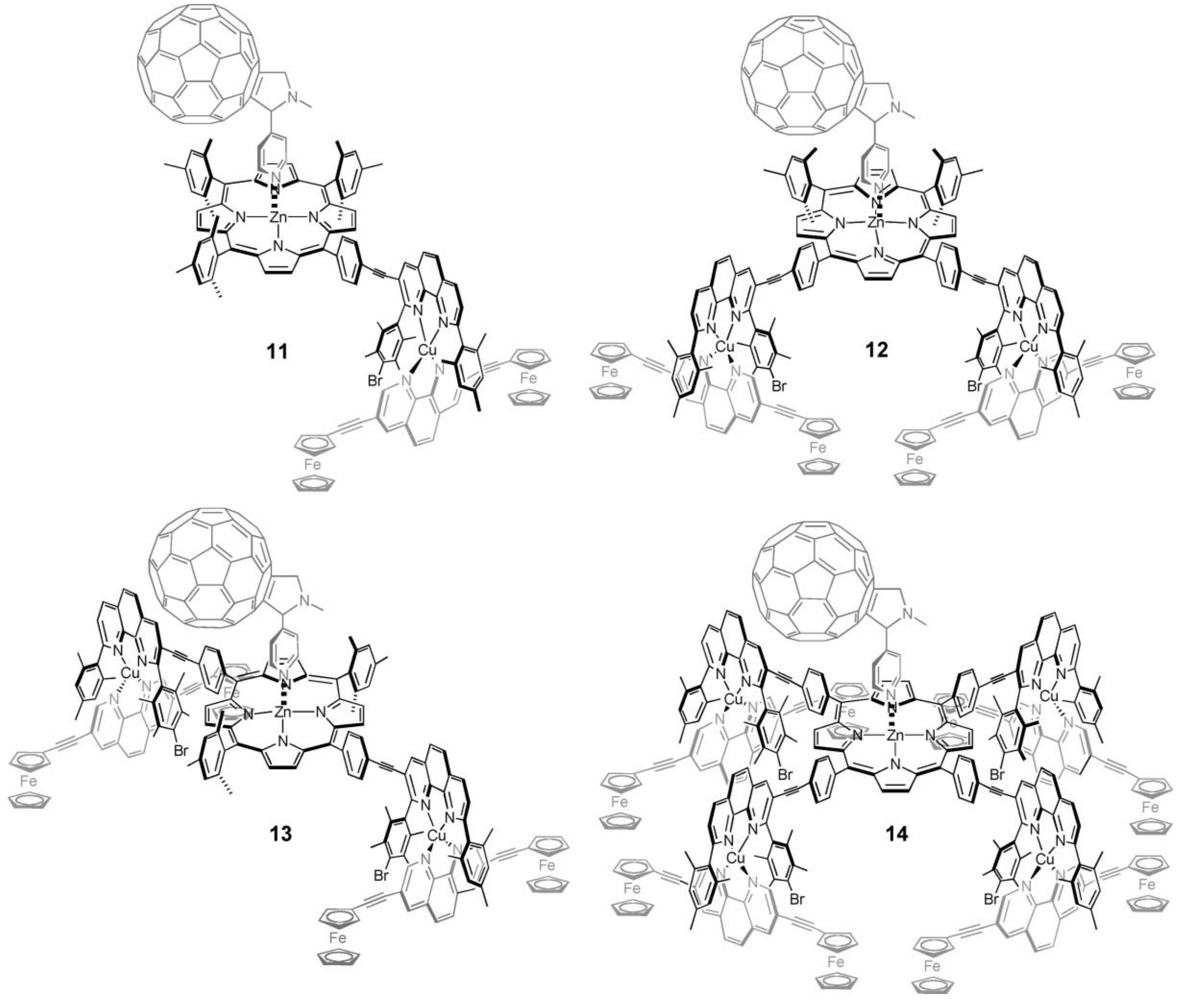

Chart 2 Chemical representation of tetrads **11–14**.

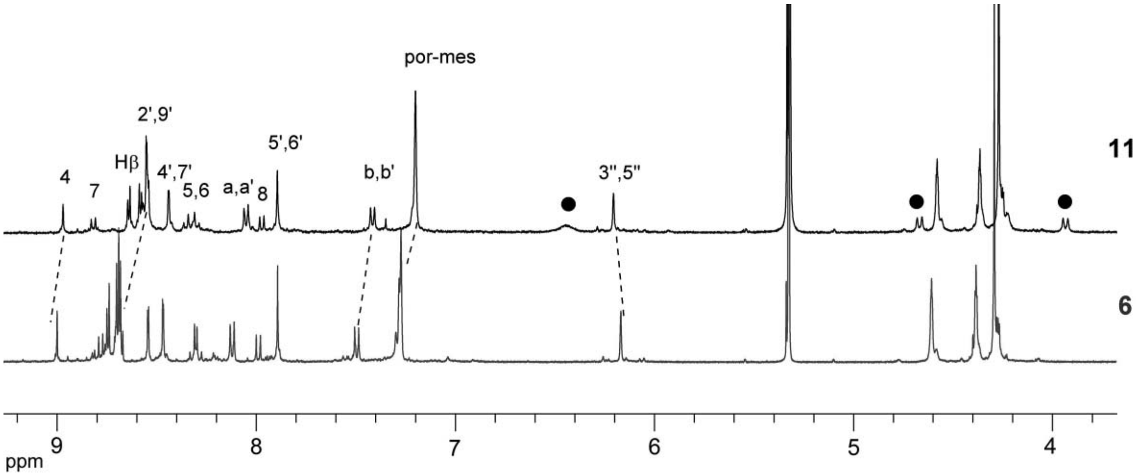

Fig. 3 Aromatic region in the ^{1}H NMR spectra of **6** and **11**. The solid black circles represent the shifts of the 3,5-H and the pyrrolidine protons.

constant for formation of **11–14** (from **6–9** and **10**) is higher by half an order of magnitude than that of **ZnTPP** and **10**.

The molecular structure of aggregate **11** calculated at the PM3 level in SPARTAN[19] showed an edge-to-edge distance of 4.1 Å between the ferrocene and the C_{60} unit, indicative of an almost complete van der Waal's contact between the ferrocene and the fullerene unit, as reported earlier by D'Souza[9a] *et al.* for other systems. This may explain the higher association constants displayed by **11–14** and the upfield-shifted signals of the ferrocene protons in the ^{1}H NMR.

Table 2 E_{0-0} energies and association constants of zinc porphyrins with **10** calculated from UV-vis titration by SPECFIT

	K/M^{-1}	logβ	E_{0-0}/eV	reference
ZnTPP[a]	7.2×10^3	3.86 (± 0.38)	—	5d
11[b]	2.1×10^4	4.34 (± 0.05)	1.96	this work
12[b]	2.3×10^4	4.36 (± 0.02)	1.96	this work
13[b]	1.6×10^4	4.19 (± 0.07)	1.96	this work
14[b]	2.6×10^4	4.42 (± 0.03)	1.96	this work

[a] Measured in *ortho*-dichlorobenzene at 298 K. [b] Measured in DCE at 298 K.

Compounds **11–14** are supramolecular aggregates built purely by a supramolecular assembly protocol by applying two dynamic non-interfering binding modes. Certainly, the heteroleptic Cu(I)–bisphenanthroline complex is a dynamic yet robust (logβ ~9.7) supramolecular motif, as we have recently shown by demonstrating the exchange of metal ions (Cu(I) *vs.* Ag(I)), as well as of ligands.[13] The latter was found to be completely arrested only at −60 °C. Axial binding of the pyridyl fullerene to zinc porphyrin (log$K$ ~4.3) is comparatively more dynamic. This is evidenced by broadened signals of the pyridyl protons in the ^{1}H NMR of **11–14** at room temperature. However, an earlier study by Imamura[20] stated that below −40 °C the dynamic nature of this system was arrested, as seen from the sharpening of the signals of the pyridyl protons in the ^{1}H NMR.

Electrochemical studies

The electrochemical properties of complexes **11–14** were investigated along with those of **1–9** (Table 3 and Table S3†). The redox potentials were measured by differential pulse voltammetry (DPV) and cyclic voltammetry in dichloroethane. The intactness of the supramolecule in the presence of electrolyte NBu_4PF_6 under the DPV and CV conditions was proven by absorption spectroscopy.

Redox data of **6–9** (Table 3) were measured in dichloroethane by differential pulse voltammetry (DPV). It was observed that the redox potentials of $P^{+/2+}$, $P^{0/+}$, $Cu^{+/2+}$ and ferrocene ($Fc^{0/+}$) in **6–9** were not influenced by the number of phenanthrolines at the porphyrin periphery. In contrast, the porphyrin reduction potential ($P^{0/-}$) exhibited an anodic shift of ~70 mV while going from **6** to **9** (Table 3). The number of electrons transferred in the individual redox steps, as analysed from the integrated areas of the DPV curves, indicated that the first oxidation of the porphyrin ($P^{0/+}$) and that of $Cu^{+/2+}$ overlapped at $E = 0.41\ V_{Fc}$. This assignment was confirmed by preparing **6a**, the silver analog of **6**, containing an Ag(I) instead of the Cu(I) phenanthroline complex. As for **6**, the porphyrin $E_{1/2}$ ($P^{0/+}$) in **6a** was located at $E = 0.41\ V_{Fc}$.

Table 3 shows the redox potentials of **11–14**. On the basis of two criteria (peak separation $E_{pa} - E_{pc}$ and $i_{pa}/i_{pc} = 1$) the redox processes were found to be reversible. In contrast to systems **6–9**, the redox waves for $Cu^{+/2+}$ and $P^{0/+}$ in **11–14** only partly overlapped, so that we could employ a peak deconvolution with PEAKFIT for their analysis. The $E_{1/2}$ ($P^{0/+}$) of the porphyrin unit in **11–14** exhibited small, but uncharacteristic shifts when compared to **6–9**, while the reduction potential $E_{1/2}$ ($P^{0/-}$) revealed cathodic shifts of 0–70 mV. The porphyrin potentials $E_{1/2}$ ($P^{0/+}$) of **11–14** are higher than that of **ZnTPP·10** by 200 mV, mostly due to the electron-withdrawing effect of the $Cu^{+/2+}$ centres and to a lesser extent because of the charged $Fc^{\bullet+}$ groups.

Due to the spatial arrangement and electrochemical data of **11–14** we expect that upon photochemical excitation of the porphyrin unit a PET process will generate $C_{60}^{\bullet-}$–$Por^{\bullet+}$–$Cu(phen)_2^{+}$–Fc, which will undergo further CS to $C_{60}^{\bullet-}$–Por–$Cu(phen)_2^{2+}$–Fc and finally to $C_{60}^{\bullet-}$–Por–$Cu(phen)_2^{+}$–$Fc^{\bullet+}$. Hence, the present system should operate as a A–D–D–D tetrad, with the CS from $C_{60}^{\bullet-}$–$Por^{\bullet+}$–$Cu(phen)_2^{+}$–Fc to $C_{60}^{\bullet-}$–Por–$Cu(phen)_2^{2+}$–Fc having almost no driving force. A caveat of the present discussion is that the redox data in Table 3 do not precisely reflect the redox situation in the photochemically triggered tetrads. Obviously, the PET process will be initiated with the ferrocene units being uncharged and the copper being singly-charged, while the data for $P^{0/+}$ recorded in Table 3 are influenced by the oxidised ferrocene and the doubly-charged copper units.

Conclusions

We have successfully established a protocol to obtain dynamic supramolecular aggregates based on two orthogonal coordinative binding motifs. The successful introduction of a $Cu(phen)_2$ redox unit into the tetrad system should facilitate stepwise charge separation, as has been noticed previously with other supramolecular CS systems.[10,11,21] Moreover, the present self-assembly approach leaves a lot of room for further fine-tuning

Table 3 Redox potentials of **6–9** and **11–14**

	$E_{1/2}$ *vs.* Fc [a]						
	$P^{+/2+}$	$P^{0/+}$, $Cu^{+/2+}$	$Fc^{0/+}$	$C_{60}^{0/-}$	$C_{60}^{-/2-}$	$P^{0/-}$	HOMO–LUMO/eV[b]
6	0.74	0.41, 0.41	0.21	—	—	−1.91	—
6a	0.74	0.41	0.21	—	—	—	—
7	0.77	0.41, 0.41	0.20	—	—	−1.86	—
8	0.74	0.41, 0.41	0.21	—	—	−1.86	—
9	0.77	0.41, 0.41	0.20	—	—	−1.84	—
11	0.85	0.37, 0.30[c]	0.21[d]	−1.06	−1.47	−1.98	1.27
12	0.83	0.42, 0.36[c]	0.21	−1.04	−1.44	−1.88	1.25
13	0.77	0.39, 0.33[c]	0.20	−1.08	−1.50	−1.88	1.28
14	0.81	0.40, 0.28[c]	0.19	−1.04	−1.44	−1.85	1.23

[a] Determined by DPV in dichloroethane with NBu_4PF_6 as electrolyte, and measured against an Ag wire as a quasi-reference electrode and dimethylferrocene as internal standard at 100 mV s^{-1}. Potentials are referenced against the more common ferrocene redox couple. [b] Determined from the redox potentials $Fc^{0/+} - C_{60}^{0/-}$. [c] Deconvolution allowed to separate the overlapping waves of the $P^{0/+}$ and $Cu^{+/2+}$ redox processes. [d] Obtained by deconvolution.

of the electronic properties of triads and tetrads, *e.g.* using other spacers in between the coordination motifs, installing different terminal redox relays and even modulating the redox properties of the intermediate copper–bisphenanthroline linkage. Further investigations on these supramolecular tetrads are underway.

Experimental

Synthesis

Starting materials **Phen1** and **P1–4** were synthesised according to known procedures.[12,14] Ligands **1**,[13b] **4**,[13a] **5**[13a] and **10**[9] were prepared according to previous reports. ^{1}H and ^{13}C NMR were measured on a Bruker Avance 400. ESI-MS were measured on a ThermoQuest LCQ Deca instrument. Typically, 25 scans were accumulated for one spectrum. All complexes were characterised by ^{1}H NMR, ^{13}C NMR, and elemental analysis. Cyclic voltammetry and differential pulse voltammetry were measured on a Parstat 2273 potentiostat.

General procedure for synthesis of 1–4. In a three-neck round-bottomed flask flushed with argon and fitted with a reflux condenser, zinc porphyrin **P1–4** was taken up in dry benzene–triethylamine (20 mL, 15 : 5). To this solution was added 3-ethynyl-2-(4-bromo-2,3,5,6-tetramethylphenyl)-9-(2,4,6-trimethylphenyl)-[1,10]phenanthroline (**Phen1**). The mixture was degassed for 30 min under a steady flow of argon. $Pd_2(dba)_3$ and $AsPh_3$ were then added as solids. The reaction was heated at 40 °C for 4 h, after which the reaction mixture was evaporated *in vacuo*. The residue obtained was dissolved in dichloromethane, washed with a solution of 2% KCN and dried over sodium sulfate. The solid obtained by evaporating the solvents was chromatographed over silica gel to give the required ligand as a violet solid. The solid was then dissolved in 1 mL of toluene and loaded over a size exclusion gel containing BioRad SX-1 Bio-Beads swollen in toluene, and run under gravity flow. The bright red fractions collected were identified as the pure product.

Using porphyrin **P1** (138 mg, 148 µmol), **Phen1** (79 mg, 148 µmol), $Pd_2(dba)_3$ (10 mg, 1.5 µmol), $AsPh_3$ (45 mg, 148 µmol). Yield of **1**: 85 mg (43%, 63 µmol); δ_H (400 MHz, CD_2Cl_2) 8.84 (d, $J = 4$ Hz, 2 H, 2,18-H_β), 8.75 (d, $J = 4$ Hz, 2 H, 3,17-H_β), 8.70 (s, 4 H, 7,8,12,13-H_β), 8.66 (s, 1 H, 4-H), 8.36 (d, $J = 8$ Hz, 1 H, 7-H), 8.16 (d, $J = 8$ Hz, 2 H, Ar-H_b,$H_{b'}$), 7.97 (br s, 2 H, 5,6-H), 7.61 (d, $J = 8$ Hz, 1 H, 8-H), 7.51 (d, $J = 8$ Hz, 2 H, Ar-H_a,$H_{a'}$), 7.29 (s, 6 H, 3‴,5‴-H), 6.98 (s, 2 H, 3″,5″-H), 2.62 (s, 9 H, 8‴,8⁗-H), 2.55 (s, 6 H, 8′,9′-H), 2.35 (s, 3 H, 8″H), 2.14 (s, 6 H, 7″,9″-H), 2.07 (s, 6 H, 7′,10′-H), 1.84 (s, 6 H, 7⁗,9⁗-H), 1.83 (s, 6 H, 7‴,9‴-H); δ_C (100 MHz, $CDCl_3$) 163.0, 161.1, 150.5, 150.3, 150.2, 149.7, 146.6, 145.5, 144.9, 142.9, 140.7, 139.7, 138.9, 138.4, 138.0, 137.7, 136.5, 135.1, 134.9, 134.2, 133.8, 132.1, 131.5, 131.1, 130.9, 130.0, 129.7, 129.3, 128.9, 128.8, 128.7, 128.0, 127.6, 127.4, 127.1, 126.1, 125.7, 122.0, 120.7, 119.2, 119.1, 96.3, 88.1, 22.2, 22.1, 21.8, 21.5, 21.4, 20.7, 18.9; ESI-MS *m/z* (%): 1335.9 (100) $[M + H]^+$; Found: C, 77.74; H, 5.68; N, 6.28. Calcd for $C_{86}H_{73}BrN_6Zn$: C, 77.32; H, 5.51; N, 6.29%.

Using porphyrin **P2** (190 mg, 187 µmol), **Phen1** (200 mg, 375 µmol), $Pd_2(dba)_3$ (18 mg, 1.9 µmol), $AsPh_3$ (57 mg, 187 µmol). Yield of **2**: 157 mg (46%, 86 µmol); δ_H (400 MHz, CD_2Cl_2) 8.93 (s, 2 H, 2,3-H_β), 8.88 (d, 2 H, $J = 4$ Hz, 7,18-H_β), 8.80 (d, $J = 4$ Hz, 2 H, 8,17-H_β), 8.75 (s, 2 H, 12,13-H_β), 8.68 (s, 2 H, 4-H), 8.33 (d, $J = 8$ Hz, 2 H, 7-H), 8.17 (d, $J = 8$ Hz, 4 H, Ar-H_b,$H_{b'}$), 7.92 (m, 4 H, 5,6-H), 7.59 (d, $J = 8$ Hz, 2 H, 8-H), 7.55 (d, $J = 8$ Hz, 4 H, Ar-H_a,$H_{a'}$) 7.31 (s, 4 H, 3‴,5‴-H), 7.00 (s, 4 H, 3″,5″-H), 2.63 (s, 6 H, 8‴-H), 2.57 (s, 12 H, 8′,9′-H), 2.37 (s, 6 H, 8″-H), 2.17 (s, 12 H, 7″,9″-H), 2.09 (s, 12 H, 7′,10′-H), 1.85 (s, 12 H, 7‴,9‴-H); δ_C (100 MHz, CD_2Cl_2) 162.7, 160.9, 150.5, 150.2, 150.1, 149.9, 146.4, 145.3, 143.9, 139.8, 139.5, 139.2, 138.9, 138.4, 138.0, 137.9, 136.5, 136.1, 134.9, 134.3, 133.9, 132.3, 131.9, 131.6, 131.3, 130.0, 129.4, 128.6, 128.0, 128.0, 127.5, 127.4, 126.0, 125.2, 122.1, 120.3, 119.9, 119.7, 95.9, 87.9, 21.8, 21.5, 21.2, 21.2, 20.5, 18.7; ESI-MS *m/z* (%): 1825.8 (90) $[M + H]^+$, 913.7 (100) $[M + 2H]^{2+}$; Found: C, 76.48; H, 5.15; N, 5.84. Calcd for $C_{116}H_{94}Br_2N_8Zn$: C, 76.33; H, 5.19; N, 6.14%.

Using porphyrin **P3** (67 mg, 86 µmol), **Phen1** (97 mg, 182 µmol), $Pd_2(dba)_3$ (21 mg, 2.2 µmol), $AsPh_3$ (26 mg, 86 µmol). Yield of **3**: 130 mg (43%, 37 µmol); δ_H (400 MHz, CD_2Cl_2–CD_3OD) 8.77 (d, 4 H, $J = 4$ Hz, 2,8,12,18-H_β), 8.67 (d, 4 H, $J = 4$ Hz, 3,7,13,17-H_β), 8.65 (s, 2 H, 4-H), 8.36 (d, $J = 8$ Hz, 2 H, 7-H), 8.13 (d, $J = 8$ Hz, 4 H, Ar-H_b,$H_{b'}$), 7.96 (m, 4 H, 5,6-H), 7.58 (d, $J = 8$ Hz, 2 H, 8-H), 7.47 (d, $J = 8$ Hz, 4 H, Ar-H_a,$H_{a'}$), 7.27 (s, 4 H, 3‴,5‴-H), 6.96 (s, 4 H, 3″,5″-H), 2.60 (s, 6 H, 8‴-H), 2.53 (s, 12 H, 7‴,9‴-H), 2.33 (s, 6 H, 8″-H), 2.12 (s, 12 H, 7′,10′-H), 2.05 (s, 12 H, 7″,9″-H), 1.81 (s, 12 H, 8′,9′-H); δ_C (100 MHz, CD_2Cl_2/CD_3OD) 161.1, 150.3, 149.9, 146.2, 145.1, 144.5, 139.8, 139.7, 139.6, 139.1, 138.3, 137.9, 137.8, 136.7, 136.1, 135.0, 134.2, 134.0, 132.1, 130.9, 129.8, 129.4, 128.6, 128.2, 127.9, 127.6, 127.5, 126.1, 125.4, 121.8, 120.6, 120.0, 119.4, 119.3, 105.7, 96.1, 87.7, 21.7, 21.4, 21.1, 21.1, 20.4, 18.6; ESI-MS *m/z* (%):1825.8 (75) $[M + H]^+$, 913.9 (100) $[M + 2H]^{2+}$; Found: C, 76.25; H, 5.31; N, 5.93. Calcd for $C_{116}H_{94}Br_2N_8Zn$: C, 76.33; H, 5.19; N, 6.14%.

Using porphyrin **P4** (105 mg, 88 µmol), **Phen1** (200 mg, 375 µmol), $Pd_2(dba)_3$ (21 mg, 2.2 µmol), $AsPh_3$ (30 mg, 98 µmol). Yield of **4**: 130 mg (51%, 46 µmol); δ_H (400 MHz, CD_2Cl_2) 8.93 (s, 8 H, 2,3,7,8,12,13,17,18-H_β), 8.63 (s, 4 H, 4-H), 8.32 (d, $J = 8$ Hz, 4 H, 7-H), 8.13 (d, $J = 8$ Hz, 8 H, Ar-H_b,$H_{b'}$), 7.89 (br s, 8 H, 5,6-H), 7.58 (d, $J = 8$ Hz, 4 H, 8-H), 7.53 (d, $J = 8$ Hz, 8 H, Ar-H_a,$H_{a'}$), 6.98 (s, 8 H, 3‴,5‴-H), 2.55 (s, 24 H, 8″,9″-H), 2.35 (s, 12 H, 8‴-H), 2.14 (s, 24 H, 7‴,9‴-H), 2.07 (s, 24 H, 7″,10″-H).; δ_C (100 MHz, CD_2Cl_2) 162.7, 160.9, 150.3, 146.4, 145.3, 143.7, 139.8, 139.0, 138.4, 137.9, 136.4, 136.1, 134.9, 134.3, 133.9, 132.3, 130.1, 129.3, 129.2, 128.6, 128.5, 128.0, 127.5, 127.4, 126.0, 125.5, 125.2, 122.3, 120.7, 120.2, 95.7, 87.9, 21.2, 21.1, 20.4, 18.6; ESI-MS *m/z* (%): 1402.9 (100) $[M + 2H]^{2+}$, 936.1 (75) $[M + 3H]^{3+}$, 702.0 (25) $[M + 4H]^{4+}$; Found: C, 74.25; H, 5.08; N, 5.80. Calcd. for $C_{176}H_{136}Br_4N_{12}Zn\cdot 2H_2O$: C, 74.43; H, 4.97; N, 5.92%.

Synthesis of ligand 5. 3,8-Dibromophenanthroline (132 mg, 390 µmol) and ferrocenyl acetylene (198 mg, 942 µmol) were placed in a Schlenk tube flushed with nitrogen. 15 mL of dry benzene and 15 mL of dry diisopropylamine were added. Subsequently $Pd(PPh_3)_4$ (45 mg, 39 µmol) and copper(I) iodide (7 mg, 39 µmol) were added under a steady flow of nitrogen. The reaction mixture was sealed with a Teflon screw cap and stirred for 48 h at 80 °C. The dark brown reaction mixture was evaporated and redissolved in dichloromethane. The dark solution was then washed with 5% KCN solution and 10% KOH, and the dichloromethane portion evaporated to give a dark brown solid. Column chromatography on silica-gel in dichloromethane–methanol afforded as the third fraction a dark orange solid, which was found to be the product. Yield of **5**: 98 mg (164 µmol, 42%); δ_H (400 MHz, $CDCl_3$) 9.21

(d, *J* = 2 Hz, 2 H, 2,9-H), 8.28 (d, *J* = 2 Hz, 2 H, 4,7-H), 7.73 (s, 2 H, 5,6-H), 4.58–4.59 (m, 4 H, 2′,2‴-H, 5′,5‴-H), 4.30–4.32 (m, 2 H, 3′,3‴,4″,4‴-H), 4.28 (br s, 10 H, 1″,2″,3″,4″,5″,1⁗,2⁗,3⁗,4⁗,5⁗-H); δ_C (100 MHz, $CDCl_3$) 152.2, 143.9, 137.4, 127.9, 126.6, 120.3, 93.7, 82.9, 71.6, 70.0, 69.3, 64.1; ESI-MS: $C_{36}H_{25}Fe_2N_2$ *m*/*z* (100%) 597.4 (100) $[M + H]^+$; Found: C, 68.43; H, 4.54; N, 4.14; Calcd. for $C_{36}H_{24}Fe_2N_2\cdot\frac{1}{2}CH_2Cl_2$: C, 68.36; H, 3.95; N, 4.39%.

General procedure for the synthesis of the aggregates 6–9. To stoichiometric amounts of the porphyrin ligand in dichloromethane, $[Cu(CH_3CN)_4]PF_6$ was added. Subsequently, stoichiometric amounts of **5** was added. The resulting solution showed an instantaneous change in colour to deep red. The complex was isolated without any further purification and obtained in quantitative yield.

Triad **6**. δ_H (400 MHz, CD_2Cl_2) 8.99 (s, 1 H, 4-H), 8.76 (d, *J* = 8 Hz, 1 H, 7-H), 8.74 (d, *J* = 4 Hz, 2 H, 2,18-H_β), 8.69 (d, *J* = 4 Hz, 2 H, 3,17-H_β), 8.66 (br s, 4 H, 7,8,12,13-H_β), 8.53 (d, ^4J = 2 Hz, 2 H, 2′,9′-H), 8.45 (d, ^4J = 2 Hz, 2 H, 4′,7′-H), 8.29 (d, *J* = 9 Hz, 1 H, 5-H), 8.26 (d, *J* = 9 Hz, 1 H, 6-H), 8.13 (d, *J* = 8 Hz, 2 H, Ar-H_a,$H_{a'}$), 7.97 (d, *J* = 8 Hz, 1 H, 8-H), 7.88 (s, 2 H, 5′,6′-H), 7.48 (d, *J* = 8 Hz, 2 H, Ar-H_b,$H_{b'}$), 7.23 (s, 6 H, 3⁗,5⁗-H), 6.16 (s, 2 H, 3‴,5‴-H), 4.57 (d, *J* = 5 Hz, 4 H, 2,5,2″,5″-H_{cp}), 4.35 (d, *J* = 3 Hz, 4 H, 3,4,3″,4″-H_{cp}), 4.26 (s, 10 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H_{cp}) 2.58 (s, 6 H, por-mes-Me), 2.56 (s, 3H, por-mes-Me), 1.95 (s, 6 H, 8″,9″-H), 1.93 (s, 6 H, 7″,10″), 1.79 (s, 12 H, por-mes-Me), 1.77 (s, 6 H, 7‴,9‴-H), 1.76 (s, 6 H, por-mes-Me),1.64 (s, 3 H, 8‴-H); δ_C (100 MHz, CD_2Cl_2) 161.3, 159.9, 150.3, 150.1, 149.9, 149.8, 144.1, 142.6, 140.8, 139.7, 139.6, 139.5, 139.4, 138.3, 138.0, 137.8, 137.7, 137.3, 135.2, 135.0, 133.9, 132.8, 131.8, 131.4, 131.3, 130.9, 130.0, 129.3, 128.6, 128.5, 128.2, 128.1, 127.9, 127.6 127.4, 127.3, 126.7, 123.3, 122.5, 120.9, 119.0, 118.7, 116.9, 98.0, 96.9, 86.1, 81.8, 72.3, 70.5, 70.3, 21.8, 21.5, 20.6, 20.4, 20.3, 18.8; ESI-MS *m*/*z* (%): 1995.7(100) $[M]^+$. Found: C, 65.88; H, 4.36; N, 5.65. Calcd for $C_{122}H_{97}BrCuF_6Fe_2N_8PZn\cdot CH_2Cl_2$: C, 66.38; H, 4.48; N, 5.03%.

Triad **7**. δ_H (400 MHz, CD_2Cl_2) 9.00 (s, 2 H, 4-H), 8.77 (d, *J* = 8 Hz, 2 H, 7-H), 8.76 (s, 2 H, 2,3-H_β), 8.73 (d, *J* = 4 Hz, 2 H, 7,18-H_β), 8.69 (d, *J* = 4 Hz, 2 H, 8,17-H_β), 8.68 (s, 2 H, 12,13-H_β), 8.53 (d, *J* = 2 Hz, 4 H, 2′,9′-H), 8.46 (s, 4 H, 4′,7′-H), 8.31 (d, *J* = 8 Hz, 2 H, 5-H), 8.28 (d, *J* = 8 Hz, 2 H, 6-H), 8.06 (d, *J* = 8 Hz, 4 H, Ar-H_a,$H_{a'}$), 7.97 (d, *J* = 8 Hz, 2 H, 8-H), 7.89 (s, 4 H, 5′,6′-H), 7.48 (d, *J* = 8 Hz, 4 H, Ar-H_b,$H_{b'}$), 7.26 (s, 4 H, 3⁗,5⁗-H), 6.16 (s, 4 H, 3‴,5‴-H), 4.60 (s, 8 H, 2,5,2″,5″-H_{cp}), 4.38 (s, 8 H, 3,4,3″,4″-H_{cp}), 4.29 (s, 20 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H_{cp}), 2.58 (s, 6 H, por-mes-Me), 1.94 (s, 12 H, 8″,9″-H), 1.93 (s, 12 H, 7″,9″-H), 1.79 (s, 12 H, 7‴,9‴-H), 1.77 (s, 12 H, por-mes-Me), 1.64 (s, 6 H, 8‴-H); δ_C (100 MHz, CD_2Cl_2), 161.2, 159.8, 150.6, 150.2, 149.9, 149.7, 144.5, 144.1, 142.6, 140.8, 139.7, 139.4, 139.0, 138.3, 138.1, 137.9, 137.7, 137.3, 135.2, 134.9, 133.9, 132.8, 131.7, 131.3, 130.1, 129.3, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 127.6, 127.4, 127.3, 126.7, 123.2, 122.5, 121.2, 119.9, 119.5, 116.9, 97.8, 96.9, 86.2, 81.8, 77.9, 72.3, 70.6, 70.4, 63.4, 21.7, 21.5, 20.6, 20.4, 20.3, 18.8; ESI-MS *m*/*z* (%): 1572.3 (100) $[M]^{2+}$ Found: C, 60.68; H, 3.93; N, 4.54 Calcd. for $C_{188}H_{142}Br_2Cu_2F_{12}Fe_4N_{12}P_2Zn\cdot 4CH_2Cl_2$: C, 61.09; H, 4.01; N, 4.45%.

Triad **8**. δ_H (400 MHz, CD_2Cl_2) 8.98 (s, 2 H, 4-H), 8.77 (d, *J* = 8 Hz, 2 H, 7-H), 8.75 (d, *J* = 4 Hz, 4 H, 2,8,12,18-H_β), 8.69 (d, *J* = 4 Hz, 4 H, 3,7,13,17-H_β), 8.49 (s, 4 H, 2′,9′-H), 8.41 (s, 4 H, 4′,7′-H), 8.29 (d, *J* = 8 Hz, 2 H, 5-H), 8.28 (d, *J* = 8 Hz, 2 H, 6-H), 8.08 (d, *J* = 8 Hz, 4 H, Ar-H_a,$H_{a'}$), 7.96 (d, *J* = 8 Hz, 2 H, 8-H), 7.86 (s, 4 H, 5′,6′-H), 7.48 (d, *J* = 7.8 Hz, 4 H, Ar-H_b,$H_{b'}$), 7.25 (s, 4 H, 3⁗,5⁗-H), 6.14 (s, 4 H, 3‴,5‴-H), 4.70 (br s, 8 H, 2,5,2″,5″-H_{cp}), 4.43 (br s, 28 H, 3,4,3″,4″-1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H_{cp}), 2.59 (s, 6 H, por-mes-Me), 1.92 (s, 12 H, 8″,9″-H), 1.90 (s, 12 H, 7″,10″-H), 1.77 (s, 12 H, 7‴,9‴-H), 1.75 (s, 12 H, por-mes-Me), 1.62 (s, 6 H, 8‴-H); δ_C (100 MHz, CD_2Cl_2) 161.3, 159.8, 149.9, 144.1, 142.6, 140.7, 139.6, 139.4, 139.0, 138.3, 138.0, 137.9, 137.7, 137.3, 135.1, 134.9, 133.9, 132.7, 132.3, 131.2, 130.2, 130.1, 129.3, 128.8, 128.6, 128.5, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 126.6, 123.2, 122.5, 121.2, 116.8, 97.0, 86.2, 81.7, 73.1, 71.8, 30.0, 21.6, 21.5, 20.6, 20.4, 20.3, 18.8; ESI-MS *m*/*z* (%): 1572.3 (100) $[M^{2+}]$; Found: C, 61.04; H, 4.08; N, 4.42; Calcd. for: $C_{188}H_{142}Br_2Cu_2F_{12}Fe_4N_{12}P_2Zn\cdot 4CH_2Cl_2$: C, 61.09; H, 4.01; N, 4.45%.

Triad **9**. δ_H (400 MHz, CD_2Cl_2) 8.99 (s, 4 H, 4-H), 8.78 (d, *J* = 8 Hz, 4 H, 7-H), 8.75 (s, 8 H, H_β), 8.51 (s, 8 H, 2′,9′-H), 8.44 (s, 8 H, 4′,7′-H), 8.30 (br s, 8 H, 5,6-H), 8.02 (d, *J* = 8 Hz, 8 H, Ar-H_a,$H_{a'}$), 7.98 (d, *J* = 8.0 Hz, 4 H, 8-H), 7.88 (s, 8 H, 5′,6′-H), 7.46 (d, *J* = 8 Hz, 8 H, Ar-H_b,$H_{b'}$), 6.14 (s, 8 H, 3‴,5‴-H), 4.64 (s, 16 H, 2,5,2″,5″-H_{cp}), 4.42 (s, 16 H, 3,4,3″,4″-H_{cp}), 4.32 (s, 40 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H_{cp}), 1.92 (s, 48 H, 7″,8″,9″,10″-H), 1.76 (s, 24 H, 7‴,9‴-H), 1.63 (s, 12 H, 8‴-H); δ_C (100 MHz, CD_2Cl_2) 161.1, 159.7, 150.1, 149.9, 144.1, 142.6, 140.7, 139.8, 139.4, 138.3, 137.9, 137.6, 137.4, 135.1, 134.8, 133.8, 132.7, 132.2, 130.1, 129.2, 128.6, 128.5, 128.1, 128.0, 127.6, 127.4, 126.7, 126.7, 123.1, 122.4, 116.8, 97.5, 96.9, 86.2, 81.8, 72.8, 71.1, 30.0, 20.6, 20.4, 20.3, 18.8; ESI-MS *m*/*z* (%): $[M]^{4+}$ 1360.5 (100); Found: C, 60.76; H, 4.16; N, 4.47; Calcd. for $C_{320}H_{232}Br_4Cu_4F_{24}Fe_8N_{20}P_4Zn\cdot 4CH_2Cl_2$: C, 61.16; H, 3.80; N, 4.40%.

General procedure for the synthesis of the aggregates 11–14. To stoichiometric amounts of the porphyrin–Cu(phen)$_2$–ferrocene aggregates in dichloromethane, a solution of the fullerene **10** in CS_2 was added. The resulting solution showed an instantaneous change in colour to greenish-brown. The complex was isolated without any further purification.

Tetrad **11**. δ_H (400 MHz, CD_2Cl_2–CS_2) 8.97 (s, 1 H, 4-H), 8.81 (d, *J* = 8 Hz, 1 H, 7-H), 8.63 (d, *J* = 4 Hz, 2 H, 2,18-H_β), 8.57 (d, *J* = 4 Hz, 2 H, 3,17-H_β), 8.55 (br s, 4 H, 7,8,12,13-H_β), 8.54 (d, ^4J = 2 Hz, 2 H, 2′,9′-H), 8.44 (d, ^4J = 2 Hz, 2 H, 4′,7′-H), 8.35 (d, *J* = 9 Hz, 1 H, 5-H), 8.30 (d, *J* = 9 Hz, 1 H, 6-H), 8.04 (d, *J* = 8 Hz, 2 H, Ar-H_a,$H_{a'}$), 7.96 (d, *J* = 8 Hz, 1 H, 8-H), 7.89 (s, 2 H, 5′,6′-H), 7.41 (d, *J* = 8 Hz, 2 H, Ar-H_b,$H_{b'}$), 7.20 (s, 6 H, 3⁗,5⁗-H), 6.45 (br s, 2 H, 3,5-H_{py}), 6.20 (s, 2 H, 3‴,5‴-H), 4.66 (d, *J* = 9 Hz, 1 H, pyr-H5$_a$), 4.58 (s, 4 H, 2,5,2″,5″-H_{cp}), 4.56 (s, 2 H, pyr-H2), 4.36 (s, 4 H, 3,4,3″,4″-H_{cp}), 4.27 (s, 10 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H_{cp}), 3.92 (d, *J* = 9 Hz, 1 H, pyr-H5$_b$), 2.59 (s, 9 H, por-mes-Me), 1.97 (s, 6 H, 8″,9″-H), 1.93 (s, 6 H, 7″,10″-H),1.82 (s, 6 H, 7‴,9‴-H), 1.73 (s, 18 H, por-mes-Me), 1.71 (s, 3 H, 8‴-H), 1.27 (s, 3 H, N–CH_3–C_{60}); δ_C (100 MHz, CD_2Cl_2) 206.1, 192.8, 161.0, 159.6, 155.8, 153.5, 151.8, 151.2, 149.9, 149.8, 149.6, 149.3, 147.4, 146.3 (2), 146.2, 146.0, 145.7, 145.5(2), 145.4, 145.3, 145.2, 145.1, 144.7, 144.5, 144.4, 144.3, 144.0, 143.1, 143.0, 142.7, 142.6, 142.5, 142.2 (2), 142.1, 142.0, 141.9, 141.8, 141.7, 141.6, 141.5, 140.6, 140.2, 139.7(2), 139.6, 139.4, 139.2, 138.1, 137.8, 137.6, 137.3, 137.2, 136.7, 136.1, 135.9, 135.5, 135.0, 133.9, 132.7, 131.6, 131.2, 131.0, 130.6, 129.8, 129.2, 128.5, 128.4, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 126.6, 123.1, 122.4, 120.5, 118.7, 118.6, 118.3, 97.9, 96.7, 81.8, 80.9, 72.3, 70.5, 70.3, 54.3, 39.1, 30.8, 21.9, 21.8, 21.4, 20.3, 20.2, 18.7. Found: C, 73.85; H, 3.75; N, 4.41. Calcd. for $C_{190}H_{107}BrCuF_6Fe_2N_{10}PZn\cdot1\frac{1}{2}CH_2Cl_2$: C, 73.65; H, 3.55; N, 4.49%.

Tetrad **12**. δ_H (400 MHz, $C_2D_4Cl_2$) 8.98 (s, 2 H, 4-H), 8.75 (d, $J = 8$ Hz, 2 H, 7-H), 8.62 (s, 2 H, 2,3-H$_\beta$), 8.59 (d, $J = 4$ Hz, 2 H, 7,18-H$_\beta$), 8.54 (d, $J = 4$ Hz, 2 H, 8,17-H$_\beta$), 8.51 (s, 2 H, 12,13-H$_\beta$), 8.47 (d, $J = 2$ Hz, 4 H, 2′,9′-H), 8.44 (d, $J = 2$ Hz, 4 H, 4′,7′-H), 8.29 (d, $J = 8$ Hz, 2 H, 5-H), 8.28 (d, $J = 8$ Hz, 2 H, 6-H), 7.97 (d, $J = 8$ Hz, 4 H, Ar-H$_a$,-H$_{a'}$), 7.95 (d, $J = 8$ Hz, 2 H, 8-H), 7.85 (s, 4 H, 5′,6′-H), 7.42 (d, $J = 8$ Hz, 4 H, Ar-H$_b$,H$_{b'}$), 7.16 (s, 4 H, 3⁗,5⁗-H), 6.26 (br s, 2 H, 3,5-H$_{py}$), 6.07 (s, 4 H, 3‴,5‴-H), 4.57 (s, 8 H, 2,5,2″,5″-H$_{cp}$), 4.36 (s, 1 H, pyr-H2), 4.33 (s, 8 H, 3,4,3″,4″-H$_{cp}$), 4.24 (s, 20 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H$_{cp}$), 4.22 (d, $J = 9$ Hz, 1 H, pyr-H5$_b$), 2.52 (s, 6 H, por-mes-Me), 1.91 (s, 12 H, 8″,9″-H), 1.87 (s, 12 H, 7″,10″-H), 1.72 (s, 12 H, 7‴,9‴-H), 1.64 (s, 12 H, por-mes-Me), 1.56 (s, 6 H, 8‴-H), 1.23 (s, 3 H, N–CH_3–C$_{60}$). δ_C (100 MHz, $C_2D_4Cl_2$) 206.0, 192.7, 160.9, 159.5, 155.7, 153.4, 151.7, 151.2, 150.1, 149.9, 149.7, 149.6, 149.3, 146.2, 146.0, 145.4(2), 145.3(2), 145.2, 145.1, 145.0, 144.9, 144.6, 144.0, 142.8, 142.6, 142.5, 142.4, 142.0, 141.9, 141.8, 141.7, 141.5, 140.6, 140.1, 139.7, 139.4, 139.2, 138.1, 137.8, 137.6, 137.5, 137.2, 135.0, 133.8, 132.9, 131.8, 131.3, 130.9, 129.8, 129.1, 128.5, 128.4, 128.0, 127.9, 127.8, 127.5, 127.3, 126.6, 123.0, 122.4, 120.6, 119.3, 118.9, 97.7, 96.7, 86.2, 81.8, 72.3, 70.6, 70.3, 63.4, 54.3, 39.1, 30.8, 21.9, 21.4, 20.4, 20.3, 20.2, 18.7 ESI-MS *m/z* (%): $[M]^{2+}$ 1999.0 (20); Found: C, 65.61; H, 3.53; N, 3.97; Calcd. for $C_{256}H_{152}Br_2Cu_2F_{12}Fe_4N_{14}P_2Zn\cdot6CH_2Cl_2$: C, 65.57; H, 3.44; N, 4.09%.

Tetrad **13**. δ_H (400 MHz, $C_2D_4Cl_2$) 8.99 (s, 2 H, 4-H), 8.77 (d, $J = 8$ Hz, 2 H, 7-H), 8.63 (d, $J = 4$ Hz, 4 H, 2,8,12,18-H$_\beta$), 8.56 (d, $J = 4$ Hz, 4 H, 3,7,13,17-H$_\beta$), 8.48 (s, 4 H, 2′,9′-H), 8.45 (s, 4 H, 4′,7′-H), 8.29 (d, $J = 8$ Hz, 2 H, 5-H), 8.28 (d, $J = 8$ Hz, 2 H, 6-H), 7.98 (d, $J = 8$ Hz, 4 H, Ar-H$_a$,H$_{a'}$), 7.97 (d, $J = 8$ Hz, 2 H, 8-H), 7.87 (s, 4 H, 5′,6′-H), 7.44 (d, $J = 7.8$ Hz, 4 H, Ar-H$_b$,H$_{b'}$), 7.19 (s, 6 H, 3⁗,5⁗-H), 6.22 (br s, 2 H, 3,5-H$_{py}$), 6.08 (s, 4 H, 3‴,5‴-H), 4.63 (s, 8 H, 2,5,2″,5″-H$_{cp}$), 4.57 (d, $J = 9$ Hz, 1 H, pyr-H5$_a$), 4.45 (s, 1 H, pyr-H2), 4.38 (s, 8 H, 3,4,3″,4″-H$_{cp}$), 4.29 (s, 20 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H$_{cp}$), 3.83 (d, $J = 9$ Hz, 1 H, pyr-H5$_b$), 2.54 (s, 6 H, por-mes-Me), 1.94 (s, 12 H, 8″,9″-H), 1.89 (s, 12 H, 7″,10″-H), 1.75 (s, 12 H, 7‴,9‴-H), 1.67 (s, 12 H, por-mes-Me), 1.57 (s, 6 H, 8‴-H), 1.25 (s, 3 H, N–CH_3–C$_{60}$); δ_C (100 MHz, $C_2D_4Cl_2$) 206.1, 192.8, 160.9, 159.6, 155.8, 153.5, 149.9, 146.3, 146.2, 146.0, 145.5(2), 145.4, 145.2, 144.8, 144.5, 144.4, 144.3, 144.0, 142.8, 142.7, 142.6, 142.5, 142.2(2), 142.1, 141.8, 141.5, 140.6, 140.2, 139.7, 139.4, 139.3, 139.2, 138.1, 137.8, 137.6, 137.5, 137.2, 136.2, 135.9, 135.5, 135.0, 133.9, 132.8, 132.0, 130.8, 129.9, 129.2, 128.5, 128.4, 128.0, 127.9, 127.8, 127.5, 127.3, 127.2, 126.5, 123.0, 122.4, 120.6, 97.8, 96.7, 96.2, 81.8, 72.5, 70.8, 70.6, 54.3, 39.1, 30.8, 21.8, 21.4, 20.3, 20.2, 18.7. ESI-MS *m/z* (%): $[M]^{2+}$ 1999.5 (60); Found: C, 67.49; H, 3.65; N, 4.15. Calcd. for $C_{256}H_{152}Br_2Cu_2F_{12}Fe_4N_{14}P_2Zn)\cdot4CH_2Cl_2$: C, 67.46; H, 3.48; N, 4.24%.

Tetrad **14**. δ_H (400 MHz, CD_2Cl_2–CS_2): 8.99 (s, 4 H, 4-H), 8.78 (d, $J = 8$ Hz, 4 H, 7-H), 8.67 (s, 8 H, H$_\beta$), 8.51 (s, 8 H, 2′,9′-H), 8.44 (s, 8 H, 4′,7′-H), 8.32 (s, 8 H, 5,6-H), 7.96 (d, $J = 8$ Hz, 8 H, Ar-H$_a$,H$_{a'}$), 7.94 (d, $J = 8.0$ Hz, 4 H, 8-H), 7.89 (s, 8 H, 5′,6′-H), 7.40 (d, $J = 8$ Hz, 8 H, Ar-H$_b$,H$_{b'}$), 6.23 (br s, 2 H, 3,5-H$_{py}$), 6.18 (s, 8 H, 3‴-H, 5‴-H), 4.77 (d, $J = 9$ Hz, 1 H, pyr-H5$_a$), 4.62 (s, 16 H, 2,5,2″,5″-H$_{cp}$), 4.46 (s, 1 H, pyr-H2), 4.40 (s, 16 H, 3,4,3″,4″-H$_{cp}$), 4.30 (s, 40 H, 1′,2′,3′,4′,5′,1‴,2‴,3‴,4‴,5‴-H$_{cp}$), 3.95 (d, $J = 9$ Hz, 1 H, pyr-H5$_b$),1.94 (s, 24 H, 7″,8″-H) 1.90 (s, 24 H, 9″,10″-H), 1.78 (s, 24 H, 7‴,9‴-H), 1.68 (s, 12 H, 8‴-H), 1.28 (s, 3H, N-CH_3); δ_C (100 MHz, $C_2D_4Cl_2$) 206.0, 192.8, 149.9, 147.4, 146.2, 146.1, 145.9, 145.5, 145.3, 144.3, 142.5, 141.9, 140.6, 140.1, 139.8, 139.5, 138.1, 137.6, 137.2, 136.4, 135.9, 135.0, 134.9, 134.9, 134.1, 133.8, 132.8, 131.8, 129.8, 128.6, 128.4, 128.0, 127.9, 127.5, 127.3, 127.2, 122.4, 120.8, 96.7, 86.2, 81.8, 72.3, 70.5, 70.4, 70.3, 63.3, 54.3, 39.1, 30.8, 21.1, 20.4, 20.3, 20.2, 18.7; Found: C, 61.89; H, 3.59; N, 3.91 Calcd. for $C_{388}H_{242}Br_4Cu_4F_{24}Fe_8N_{22}P_4Zn\cdot10CH_2Cl_2$: C, C, 61.86; H, 3.42; N, 3.99%.

Acknowledgements

This publication is dedicated to Professor Dr Manfred Christl (Universität Würzburg) on the occasion of his 65th birthday. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for continued financial support.

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