DOI: 10.1002/ejoc.200901309

Synthesis of Fullerene-Stoppered Rotaxanes Bearing Ferrocene Groups on the Macrocycle

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Dedicated to Professor Saverio Florio on the occasion of his 70th birthday

Keywords: Rotaxanes / Fullerenes / Porphyrinoids / Ferrocene / Molecular shuttles / Supramolecular chemistry

The synthesis, characterisation and behaviour of a series of rotaxanes containing a fulleropyrrolidine stopper and two ferrocene moieties on the macrocycle is reported. Remarkably, the presence of large and bulky ferrocene groups does not interfere either in the synthesis or in the translocation of the macrocycle induced by π–π interactions between the macrocycle and the fullerene. The synthetic routes developed can also be applied to the preparation of rotaxane scaffolds that can be complexed to [Ru(CO)TPP] by axial coordination. Overall, the synthetic routes presented herein provide an efficient way to prepare a variety of rotaxanes and molecular shuttles with potential applications in different fields.

Introduction

Fullerenes and especially C_{60} derivatives are valuable building blocks for the preparation of materials with potential applications in different technological fields such as photovoltaics, non-linear optics, optoelectronics and medicinal chemistry.[1–4] The properties of C_{60} derive mostly from the three-dimensional extended π system that makes C_{60} an excellent electron-acceptor[5] with very low reorganisation energy[6] and thus a valuable component for the construction of molecular photovoltaic materials.[7] When C_{60} is coupled with electron-donors of different nature,[1,3,4] electron-transfer (ET) reactions can take place upon photoexcitation to give long-lived radical pairs, mimicking the key process at photosynthetic reaction centres. Also, C_{60} derivatives are known to exhibit a sizeable non-linear optical (NLO) response[8,9] as a result of their ability to delocalise charge extensively.[6] For this reason C_{60} derivatives have been widely studied with the aim of incorporating their properties into photonic devices such as optical switches, optical limiters and deflectors.[10] It has been demonstrated that the third-order NLO response of C_{60} can be enhanced through charge-transfer reactions that increase the second hyperpolarisability by the efficient delocalisation of charge.[9] The preparation and study of a vast series of C_{60}-based dyes with different donor–acceptor spatial arrangements have illustrated the dependency between molecular architecture and ET and NLO properties.

Fullerene-based donor–acceptor systems have been introduced into mechanically interlocked architectures[11,12] as they allow an intimate spatial and electronic coupling through a non-covalent (mechanical) bond,[13–16] which at the same time permits the study of the effect of particular donor–acceptor geometries. In these supramolecular systems a fullerene electron-acceptor supported in one submolecular fragment is coupled with an electron-donor supported in the second component (porphyrin,[17–23] phthalocyanine,[24,25] ferrocene,[26–28] extended tetrathiafulvalene[29] and aromatic amines[30]). Upon photoexcitation, long-lived radical pairs have been observed. Among such mechanically interlocked architectures, rotaxanes present the same structure as that of an abacus: a macrocycle locked onto a molecular thread by two bulky stoppers. Because both components are mechanically bonded, the macrocycle can be subjected to several types of submolecular motion such as "shuttling" (translation of the macrocycle along the thread), "pirouetting" (rotation of the macrocycle about a fixed axis) and "rocking" (changes in the orientation of the macrocycle's plane).

In recent years we have become interested in the properties of rotaxanes equipped with fullerene stoppers and ferrocene electron-donors. In a series of articles we have shown that fullerenes are not simply electro- and/or photoactive stoppers,[31–33] but, more importantly, that they can be used

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901309.

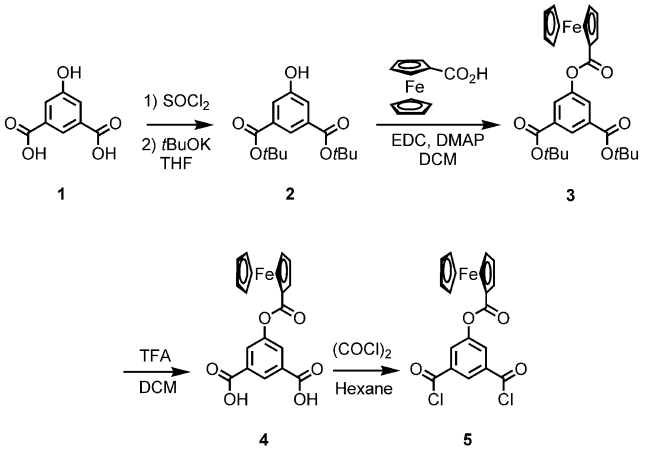
to induce a large-amplitude translational motion[34–37] between two distinct positions of the thread (stations). In such bistable rotaxanes (molecular shuttles), two well-defined and distant co-conformations can be achieved electrochemically or by a solvent change.[34–37] Because such a submolecular rearrangement also implies a change of geometry of the two components (thread and macrocycle) of the rotaxane, it seemed reasonable that by inserting an electron-donor onto the macrocycle and displacing it along the thread with respect to the fullerene electron-acceptor, it should be possible to modulate both the ET and the NLO response. In a preliminary account[35] we demonstrated that ET can be tuned by placing the macrocycle equipped with two ferrocene electron-donors at different positions along a thread equipped with a fullerene stopper. We later also demonstrated that the switchable behaviour of such systems can also be used to modulate the NLO response of the fullerene stopper.[37] Taking advantage of our knowledge of the synthesis of rotaxanes equipped with donor–acceptor moieties, we also reported a rotaxane scaffold used to organise three photo/electroactive units along a supramolecular redox gradient and we observed a two-electron-transfer cascade after photoexcitation.[38] Herein, we report in detail the design, synthesis and characterisation of such fullerene-stoppered rotaxanes bearing ferrocene electron-donors on the macrocycle.

Results and Discussion

Synthesis of Rotaxane Dyads

Our main purpose was to synthesise fullerene-stoppered rotaxanes bearing electron-donors on the macrocycle in order to study ET between the two interlocked components and any other properties that might arise from electron transfer such as NLO properties. Leigh-type rotaxanes[39] are particularly attractive for this purpose because they are not built from chromophores or redox groups and are thus the perfect scaffolds for studying the interactions between different photo- and electroactive components.

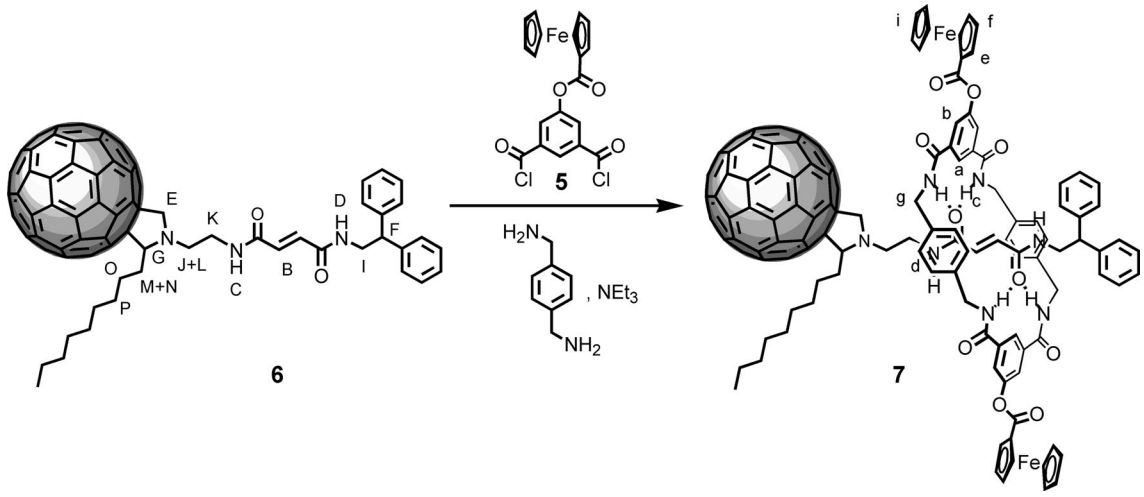
We began our research with the preparation of macrocycle precursors that would allow us to introduce electron-donors onto the macrocycle. Leigh's protocol relies on the addition under high-dilution conditions of isophthaloyl chloride and *p*-xylylenediamine to clip the macrocycle around the thread. Hence, we decided to use an isophthalic acid derivative with a hydroxy group at the 5-position to maintain the symmetry of the macrocycle and avoid the formation of different regioisomers. Typically, the conditions require at least 9 equiv. of each of the macrocycle precursors. Therefore we had to rely on a stable electron-donor that can be easily processed. Ferrocenecarboxylic acid is commercially available, reasonably cheap for working on a multigram scale and is red, which facilitates purification. The route begins with the conversion of 5-hydroxyisophthalic acid (**1**) into 5-hydroxyisophthaloyl chloride by heating at reflux in $SOCl_2$ under argon without the need of protecting the hydroxy group (Scheme 1).[40] The resulting isophthaloyl chloride was then treated with an excess of *t*BuOK to yield the *tert*-butyl isophthalate **2** in 57% yield after extraction without the need of column chromatography. Then **2** was esterified with ferrocenecarboxylic acid, which had been activated in situ by using EDC and DMAP, to give **3**. Again the purification of **3** was easily achieved by simple extraction to give very high yields (93%). The acid groups were deprotected quantitatively under acidic conditions to give acid **4**, which was subsequently transformed into 5-ferroceneacetoxyisophthaloyl chloride (**5**) in very high yield (94%) in the presence of oxalyl chloride and DMF. Acyl chloride **5** was used immediately to prepare the rotaxane (see below).



Scheme 1. Synthesis of the macrocycle precursor with a ferrocene moiety.

The precursors of the macrocycle being available, we proceeded to synthesise different molecular threads bearing the fullerene moiety. An advantage of C_{60} is its large size, which makes it an excellent electroactive stopper. The ring-closure of the benzylic amide macrocycle is assisted by a 1,4-diamide template previously introduced between the stoppers, which directs the five-component clipping reaction by hydrogen-bond recognition.[39] A clear advantage of Leigh et al.'s protocol is that a variety of 1,4-diamide templates can be used to clip the macrocycle; these templates display different affinities for the macrocycle (fumaramide >> succinamide > glycylglycine).[41,42]

To understand whether we could synthetically prepare rotaxanes bearing large substituents on the macrocycle we tested the rotaxane-forming reaction with thread **6**[32] (Scheme 2). The synthesis of thread **6** relies on the 1,3-dipolar cycloaddition of azomethine ylides to C_{60}.[43] An advantage of this method is that the resulting fulleropyrrolidines present a higher stability in comparison with other fullerene adducts, which allows the detailed study of their electrochemical properties. We used fumaramide templates as they are known to give the highest yields in rotaxane-forming reactions.[42] The excellent arrangement and rigidity of the hydrogen-bond recognition sites endow the fumaramide groups with a strong affinity for the macrocycle. The lack of solubility of the combination of C_{60} and fumaramide in the solvents necessary for the rotaxane-forming



Scheme 2. Synthesis of the C_{60}-stoppered rotaxane **7** with two ferrocene moieties on the macrocycle.

reactions was overcome by the introduction of a solubilising lateral chain in the cycloaddition step.[32] Then freshly prepared **5** and *p*-xylylenediamine (10 equiv. each) were added to **6** under high-dilution conditions in the presence of NEt_3 to give a mixture of the desired rotaxane **7** and unreacted thread **6** (Scheme 2). Rotaxane **7** was separated from thread **6** by column chromatography and purified by reprecipitation. The yields were low (12%) in comparison with an analogous rotaxane prepared without ferrocene substituents (25%)[32] because of the difficult chromatographic separation due to the close proximity of the thread and the rotaxane during elution.

The ^{1}H NMR spectrum of **7** shows typical features of a fumaramide rotaxane[42] (Figure 1a and b): the protons B (the assignments correspond to those shown in Scheme 2) in **7** is shielded by the benzylic amide rings of the macrocycle relative to the protons of thread **6**, which confirms that the macrocycle is positioned over the fumaramide template. Even though the solubility was enhanced by the presence of the two ferrocene groups, we could not obtain a ^{13}C NMR spectrum with a sufficiently good signal/noise ratio to analyse. The $[M + H]^+$ ion of **7** was detected by MALDI-TOF MS and the formation of the fulleropyrrolidine monoadduct was confirmed by UV/Vis spectroscopy.

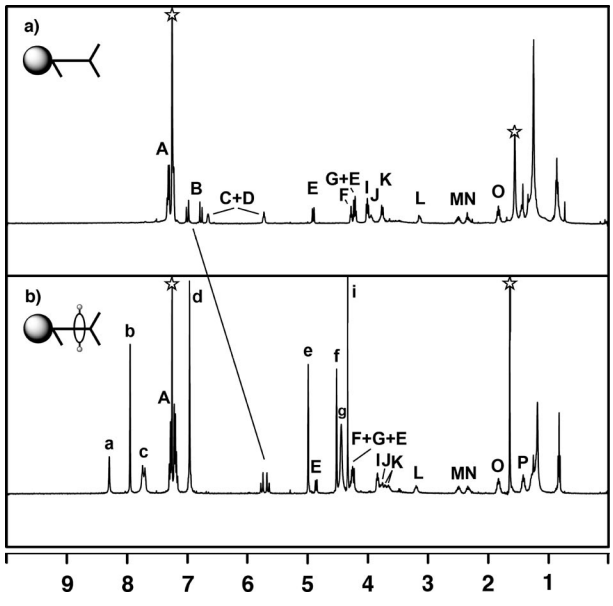
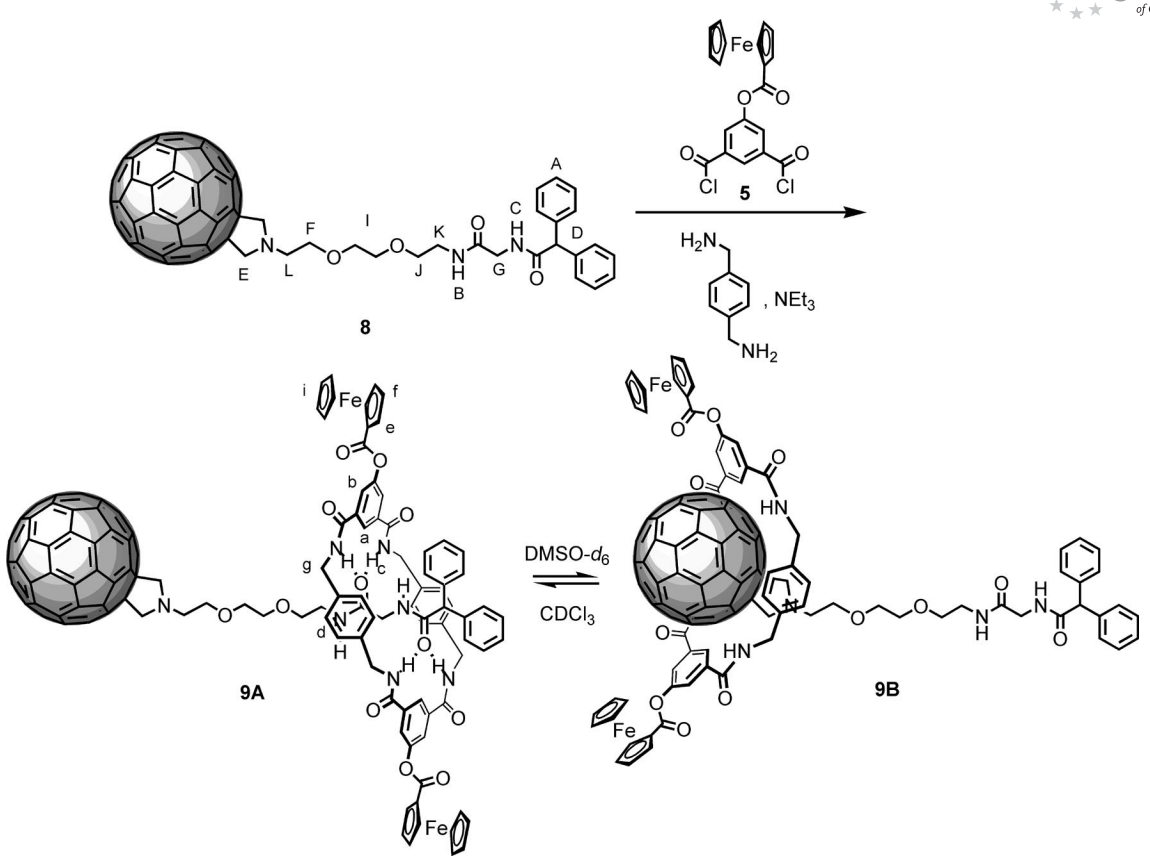


Figure 1. ^{1}H NMR (400 MHz) spectra of a) thread **6** in $CDCl_3$ and b) rotaxane **7** in $CDCl_3$. The assignments correspond to the lettering shown in Scheme 2.

Synthesis of Bistable Rotaxane Dyads

After the successful formation of **7**, we decided to test whether the large ferrocene substituent of **5** would also undergo the rotaxane-forming reaction when using templates with a lower affinity for the macrocycle than fumaramide. Dipeptidic templates possess a moderate affinity for the macrocycle because the hydrogen-bonding sites are not rigid and intramolecular hydrogen bonds can form. An advantage of using weaker templates is that they allow the decomplexation of the macrocycle under certain conditions and thus the templates can be used to prepare bistable rotaxanes or molecular shuttles.[44] We have reported a series of molecular shuttles[34,36,45] in which the shuttling is induced by π–π interactions between the fullerene and the macrocycle in the presence of dipeptidic and succinamide templates. For this reason, we decided to test the rotaxane-forming reaction with a weak template and, more importantly, to assess whether shuttling, which is effected by π–π interactions between the fullerene stopper and the macrocycle, can take place if the macrocycle bears large and bulky ferrocene groups. We chose to carry out the rotaxane-forming reaction with thread **8**,[36] which is comprised of a fulleropyrrolidine stopper, a triethylene glycol spacer, a dipeptide and a diphenyl stopper. After the addition of 5-ferrocene-acetoxyisophthaloyl chloride (**5**) and *p*-xylylenediamine to thread **8** under high-dilution conditions followed by chromatographic purification, we obtained the desired rotaxane **9** in 22% yield (Scheme 3).



Scheme 3. Synthesis and behaviour of the molecular shuttle **9**.

The ^{1}H NMR spectrum of rotaxane **9** (Figure 2b) confirmed its structure, showing typical features of dipeptide rotaxanes.[36,39] In addition, a ^{13}C NMR spectrum with a suitable signal/noise ratio was recorded for the first time because of the high solubility of rotaxane **9**. The $[M + H]^+$ ion of **9** was detected by MALDI-TOF MS and signals corresponding to a fulleropyrrolidine monoadduct were observed by UV/Vis spectroscopy. The solvent-dependency of

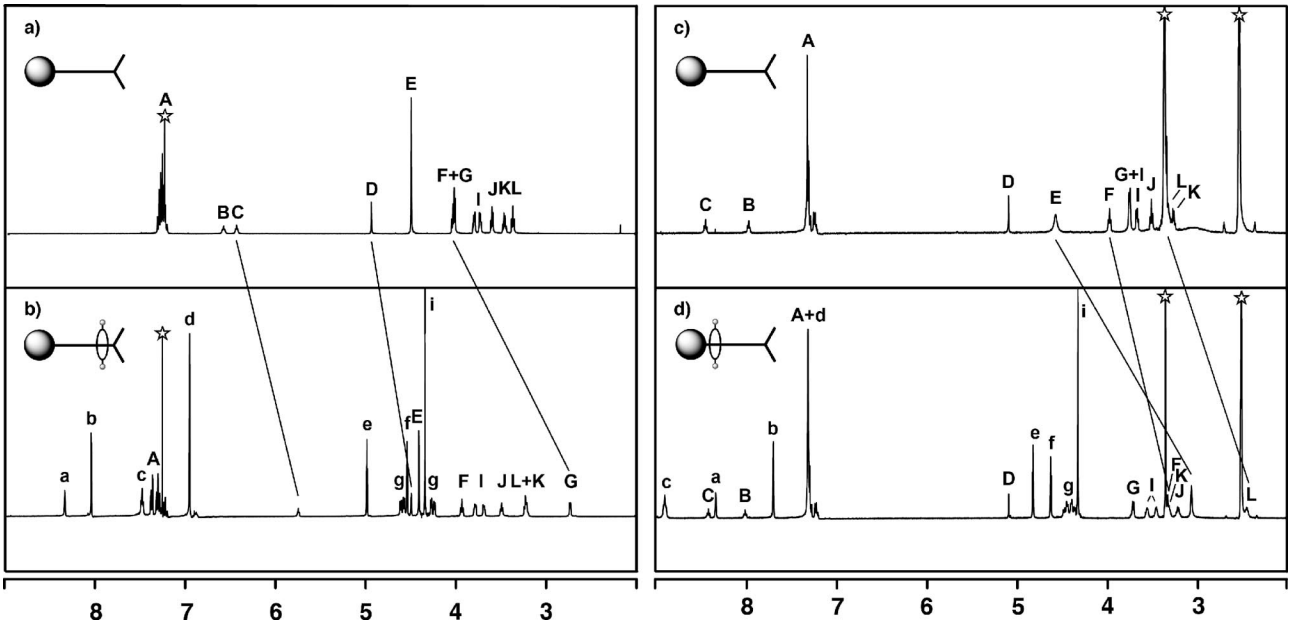


Figure 2. ^{1}H NMR (400 MHz) spectra of a) thread **8** in $CDCl_3$, b) rotaxane **9** in $CDCl_3$, c) thread **8** in $[D_6]$DMSO and d) rotaxane **9** in $[D_6]$DMSO. The peaks highlighted with stars correspond to residual solvent peaks. The assignments correspond to the lettering shown in Scheme 3.

the structure of **9** was investigated by NMR spectroscopy: rotaxane **9** was found to exist in different co-conformations in different solvents (see Figure 2). In relatively non-polar solvents (i.e., $CDCl_3$), protons G, C and D (Figure 2, a and b) are shielded in rotaxane **9** in comparison with those of thread **8**, which confirms that the macrocycle is located primarily over the peptidic residue (co-conformer **9A**). In highly polar solvents (i.e., [D_7]DMF and [D_6]DMSO), the hydrogen bonds are weakened, thereby promoting the formation of π-stacking interactions between the macrocycle and the fullerene.[34–36] Therefore the macrocycle shuttles to the opposite end of the thread, preferentially adopting the stacked co-conformation **9B**, which is reflected by the shielding of protons E, L and F (Figure 2, c and d). Remarkably, the presence of bulky ferroceneacetoxy groups on rotaxane **9** has no effect on the shuttling efficiency of the macrocycle, which behaves exactly as an analogous rotaxane with no ferrocene on the macrocycle.[36]

Supramolecular Triads

Electron transfer is not limited to donor–acceptor couples (dyad). An elegant strategy in the development of artificial reaction centres involves the coupling of C_{60} to several electron donors, typically, tetraphenylporphyrin (TPP), metalloporphyrin (MTPP) and/or ferrocene (Fc), carefully arranged.[46–48] A key factor is the organisation of the electron-donating/accepting units following an electrochemical gradient, which promotes a unidirectional charge-transfer cascade. Two consecutive charge-transfer reactions have previously been observed between Fc–TPP–C_{60} triads linked covalently and organised in that specific order.[47] Motivated by these results, we chose to insert supramolecularly an additional electron mediator into our rotaxane dyads to investigate whether the electrochemical gradient approach could also be applied to supramolecular systems. Taking into account the redox states of C_{60} and ferrocene units, their spatial arrangement and the behaviour of covalent Fc–TPP–C_{60} triads,[47] it was necessary to insert a TPP between the macrocycle with the ferrocene moieties and the C_{60} stopper. An advantage of MTPP is that it combines the electronic properties of TPP with the ability to form complexes typical of organometallic compounds. For instance, C_{60}-pyridine ligands form 1:1 complexes with MTPP by axial coordination, giving supramolecular dyads.[49–52] The 1,3-dipolar cycloaddition of azomethine ylides[43] provides a straightforward way to functionalise C_{60} with a triethylene glycol linker with a terminal-protected amine and a pyridine ligand (**10**).[53] Building block **10** has the groups necessary for assembling the triad: the pyridyl ligand and a terminal amine. The long and flexible triethylene glycol spacer was chosen to reduce the steric hindrance that might affect the bulky macrocycle functionalised with two ferrocene groups. Deprotection of the amine in **10** followed by the introduction of the template by amidation using **11**[44] gave thread **12**. Addition of 5-ferroceneacetoxyisophthaloyl chloride (**5**) and *p*-xylylenediamine to thread **12** followed by chromatography to separate unreacted thread **12** yielded rotaxane **13** in 17% yield. Surprisingly, rotaxane **13** eluted before thread **12** in the chromatographic conditions used. The ^{1}H NMR spectrum of rotaxane **13** shows typical features of dipeptidic rotaxanes (Figure 3, b); protons D, I and L (the assignments correspond to the lettering shown in Scheme 4) are shielded by the benzylic amide rings of the macrocycle by 0.9, 0.5 and 1.2 ppm when compared with those of thread **12**, which confirms that the macrocycle is positioned over the dipeptide template.[36,39] Once again we recorded a ^{13}C NMR spectrum of rotaxane **13** suitable for analysis due to its high solubility. Additional confirmation of the structure came from the detection of the $[M + Na]^+$ ion by MALDI-TOF MS and from signals corresponding to fulleropyrrolidine monoadducts observed by UV/Vis spectroscopy.

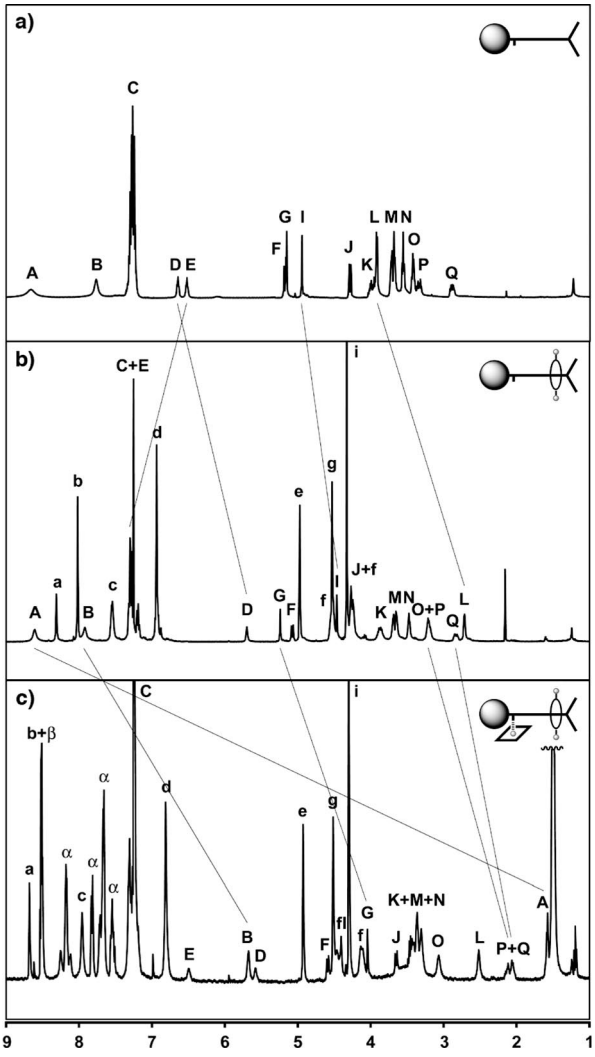
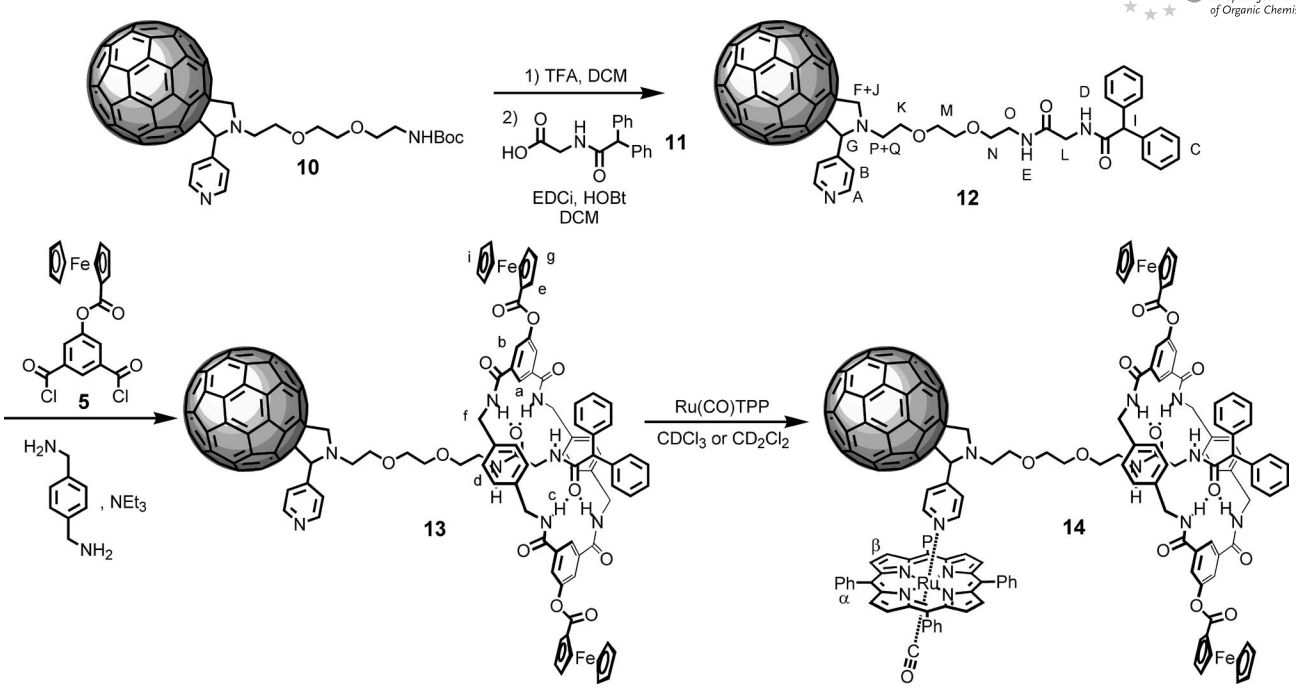


Figure 3. ^{1}H NMR (400 MHz) spectra of a) thread **12**, b) rotaxane **13** and c) triad **14** in $CDCl_3$. The assignments correspond to the lettering shown in Scheme 4.

An MTPP can be complexed to rotaxane **13** by axial coordination through the pending pyridyl group in non-coordinating solvents. In our study we used ruthenium tetra-



Scheme 4. Synthesis of supramolecular triad **14**.

phenylporphyrin [Ru(CO)TPP] as the Ru–N σ-coordination bond is reinforced by π-back-bonding to give robust supramolecular dyads.[51] The addition of 1 equiv. of [Ru(CO)-TPP] to a solution of the rotaxane **13** in $CDCl_3$ or CD_2Cl_2 resulted in the shielding of protons A, B, G, P and Q by 7.1, 2.2, 1.2, 1.1 and 0.8 ppm, respectively, which evidences the formation of triad **14** (Figure 3). This shielding is consistent with previous observations[49–52] and is an effect of the anisotropy of the porphyrin macrocycle over the protons A, B, G, P and Q that is a consequence of their proximity to the flat porphyrin surface by coordination.

Conclusions

We have reported the synthesis, characterisation and behaviour of a series of rotaxanes containing a fulleropyrrolidine stopper and two ferrocene moieties on the macrocycle. The rotaxanes were synthesised by using a modification of Leigh's protocol for the preparation of benzylic amide rotaxanes based on the introduction of a ferroceneacetoxy group on the isophthalic precursor of the benzylic amide macrocycle. Taking into account the large amounts of macrocycle precursors required for this procedure, we have developed a multigram-scale route for the preparation of 5-ferroceneacetoxyisophthaloyl chloride that can be applied to the insertion of other functional groups. The use of 5-ferroceneacetoxyisophthaloyl chloride is compatible with strong (fumaramide) and weak (dipeptidic) templates. Remarkably, the presence of large and bulky ferrocene groups does not interfere in either the synthesis or the translocation of the macrocycle induced by π–π interactions between the macrocycle and the fullerene. The routes developed can also be applied to the preparation of rotaxane scaffolds that can be complexed to [Ru(CO)TPP] by axial coordination. Overall, the synthetic routes presented herein provide an efficient way to prepare a variety of rotaxanes and molecular shuttles with potential applications in different fields.

Experimental Section

General: NMR spectra were recorded with a Varian Gemini-200 (200 MHz) or JEOL (400 MHz) spectrometer at room temperature. Chemical shifts are reported in ppm and referenced to residual solvent peaks. The NMR assignments of rotaxanes **7**, **9** and **13** correspond to the lettering shown in Schemes 2, 3 and 4, respectively. Infrared spectra were recorded with a Jasco FTIR-200 spectrometer. Mass Spectroscopy: MALDI-TOF experiments were recorded at the Université Louis Pasteur. UV/Vis/NIR spectra were recorded with a Varian 5000 UV/Vis/NIR spectrometer. Commercial compounds were used as received. EDC: *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride; HOBt: 1-hydroxybenzotriazole hydrate; DMAP: 4-(dimethylamino)pyridine; DCM: dichloromethane. Acid chloride **5** was freshly prepared before the rotaxane synthesis.

***tert*-Butyl 5-Hydroxyisophthalate (2):** $SOCl_2$ (5 mL) was added to a solution of 5-hydroxyisophthalic acid (3 g, 16.47 mmol) in THF (anhydrous, 40 mL) and heated at reflux under argon for 3 h. The solvent was removed under vacuum and the residue was dissolved in THF (anhydrous, 50 mL), which was added dropwise to a solution of *t*BuOK (9.25 g, 65.89 mmol) in THF (anhydrous, 50 mL) under argon (**CAUTION**: exothermic reaction). The remaining solution was stirred overnight. Then water (250 mL) was added in small portions to quench the excess *t*BuOK (**CAUTION**: exothermic reaction). The solution was then extracted with AcOEt. The organic phase was washed with aqueous HCl (3.5%, 2×), aqueous $NaHCO_3$ (50% water-diluted saturated solution, 2×) and brine (1×). The organic phase was dried with $MgSO_4$ and the solvent was evaporated to give the title compound (2.757 g, 57%); m.p.

123–125 °C. ^{1}H NMR ($CDCl_3$): δ = 8.13 (t, J = 1.4 Hz, 1 H, Ar), 7.77 (d, J = 1.4 Hz, 2 H, Ar), 7.08 (br. s, 1 H, OH), 1.59 (s, 18 H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$): δ = 165.25, 159.21, 133.25, 122.44, 120.44, 82.00, 28.15 ppm. MS (ES): calcd. for $C_{16}H_{22}O_5$ $[M]^+$ 294.3; found 294.9.

***tert*-Butyl 5-Ferroceneacetoxyisophthalate (3):** EDC (1.360 g, 6.88 mmol) was added in small portions to a solution of compound **2** (2.026 g, 6.88 mmol), ferroceneacetic acid (1.583 g, 6.88 mmol) and DMAP (0.840 g, 6.88 mmol) in DCM (160 mL). The solution was stirred at room temperature for 24 h. Then the solution was taken up in AcOEt and washed with aqueous HCl (3.5%, 2×), aqueous $NaHCO_3$ (50% water-diluted saturated solution, 2×) and brine (1×). The organic phase was dried with $MgSO_4$ and the solvent was evaporated to give the title compound (3.256 g, 93%); m.p. 142–144 °C. ^{1}H NMR ($CDCl_3$): δ = 8.47 (t, J = 1.5 Hz, 1 H, Ar), 7.92 (d, J = 1.5 Hz, 2 H, Ar), 4.95 (t, J = 1.8 Hz, 2 H, Fc), 4.52 (t, J = 1.8 Hz, 2 H, Fc), 4.32 (s, 5 H, Fc), 1.60 (s, 18 H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$): δ = 164.09, 150.65, 133.53, 127.52, 126.66, 81.92, 72.16, 70.65, 70.01, 28.13 ppm. MS (ES): calcd. for $C_{27}H_{30}FeNaO_6$ $[M + Na]^+$ 529.1; found 529.0.

5-Ferroceneacetoxyisophthalic Acid (4): Trifluoroacetic acid (25 mL) was added to a solution of **3** (4.210 g, mmol) in DCM (200 mL). The resulting solution was stirred at room temperature for 24 h. Evaporation of the solvent under vacuum gave the title compound in a quantitative yield; m.p. 210 °C (decomposition). ^{1}H NMR (CD_3OD): δ = 8.56 (t, J = 1.5 Hz, Ar), 8.01 (d, J = 1.5 Hz, 2 H, Ar), 5.00 (br. t, 2 H, Fc), 4.63 (br. t, 2 H, Fc), 4.36 (s, 5 H, Fc) ppm. ^{13}C NMR (CD_3O_3): δ = 177.85, 167.76, 152.35, 133.97, 128.86, 128.09, 73.65, 71.78, 71.17 ppm. MS (ES): calcd. for $C_{19}H_{14}FeNaO_6$ $[M + Na]^+$ 417.0; found 417.1.

5-Ferroceneacetoxyisophthaloyl Chloride (5): Oxalyl chloride (5 mL) was slowly added to a dispersion of **4** (500 mg, mmol) in hexane (50 mL) in the presence of DMF (0.1 mL). The dispersion was stirred overnight under argon and turned into a red solution. The solution was filtered through cotton and the solvent was evaporated under vacuum to yield the title compound (500 mg, 94%), which was used immediately after preparation. ^{1}H NMR ($CDCl_3$): δ = 8.74 (t, J = 1.6 Hz, 1 H, Ar), 8.23 (d, J = 1.6 Hz, 2 H, Ar), 4.98 (t, J = 1.7 Hz, 2 H, Fc), 4.57 (t, J = 1.7 Hz, 2 H, Fc), 4.33 (s, 5 H, Fc) ppm.

Rotaxane 7: A solution of *p*-xylylenediamine (176 mg, 1.290 mmol) in chloroform (anhydrous, stabilised with amylenes, 40 mL) and a separate solution of **5** (556 mg, 1.290 mmol) in chloroform (anhydrous, stabilised with amylenes, 40 mL) were added simultaneously over 4 h to a stirred solution of thread **6**[32] (176 mg, 0.145 mmol) in $CHCl_3$ (anhydrous, stabilised with amylenes, 70 mL) containing NEt_3 (0.4 mL, 2.573 mmol) under argon. After the addition, the reaction mixture was stirred overnight at room temperature. The solution was filtered through Celite and concentrated to dryness. Rotaxane **7** (37 mg, 12%) was separated from the unreacted thread **6** by chromatography (DCM/$CHCl_3$, 1:2) followed by reprecipitation ($CHCl_3$/diethyl ether, ×3). ^{1}H NMR ($CDCl_3$): δ = 8.30 (s, 2 H, a), 7.96 (s, 4 H, b), 7.74 (br. s, 2 H, c), 7.70 (br. s, 2 H, c), 7.31–7.16 (m, 12 H, A + C + D), 6.97 (s, 8 H, d), 5.77 (d, J = 15 Hz, 1 H, B), 5.67 (d, J = 15 Hz, 1 H, B), 5.00 (t, J = 2 Hz, 8 H, e), 4.87 (d, J = 10 Hz, 1 H, E), 4.53 (t, J = 2 Hz, 8 H, f), 4.45 (br. s, 8 H, g), 4.34 (s, 10 H, i), 4.25–4.19 (m, 3 H, F + G + E), 3.90–3.59 (m, 5 H, I + J + K), 3.26–3.14 (m, 1 H, L), 2.57–2.49 (m, 1 H, M), 2.39–2.27 (m, 1 H, N), 1.90–1.78 (m, 2 H, O), 1.48–1.36 (m, 2 H, P), 1.35–1.11 (m, 10 H, alkyl), 0.82 (t, J = 7 Hz, 3 H, CH_3) ppm. MS (MALDI-TOF): calcd. for $C_{146}H_{93}Fe_2N_7O_{10}$ $[M + H]^+$ 2217.03; found 2217.2. IR (NaCl): $\tilde{\nu}$ = 3275.0, 2921.6, 2851.7, 1733.7, 1623.3, 1522.6, 1452.1, 1424.2, 1322.0, 1264.1, 1123.3, 1091.0, 1021.6, 819.1, 756.9, 700.0 cm^{-1}. UV/Vis (THF): λ_{max} = 255, 317, 431, 704 nm.

Rotaxane 9: A solution of *p*-xylylenediamine (251 mg, 1.842 mmol) in chloroform (anhydrous, stabilised with amylenes, 40 mL) containing NEt_3 (0.27 mL, 3.684 mmol) and a separate solution of **5** (761 mg, 1.842 mmol) in chloroform (anhydrous, stabilised with amylenes, 40 mL) were added simultaneously over 4 h to a stirred solution of thread **8** (169 mg, 0.147 mmol) in $CHCl_3$ (anhydrous, stabilised with amylenes, 25 mL) under argon. After the addition, the reaction mixture was stirred for an additional 90 min at room temperature. The solution was filtered through Celite and concentrated to dryness. Rotaxane **9** (70 mg, 22%) was separated from the unreacted thread **6** by chromatography ($CHCl_3$/MeOH, 99:1) followed by reprecipitation (DCM/petroleum ether, ×3). ^{1}H NMR ($CHCl_3$): δ = 8.37 (s, 2 H, a), 8.07 (s, 4 H, b), 7.48–7.46 (m, 4 H, c), 7.40–7.10 (m, 10 H, A), 6.98 (s, 8 H, d), 6.67–6.59 (m, 1 H, B), 5.77–5.71 (m, 1 H, C), 5.01–4.98 (m, 4 H, e), 4.67–4.58 (m, 4 H, g), 4.56–4.53 (m, 4 H, f), 4.53 (s, 1 H, D), 4.44 (s, 4 H, E), 4.36 (s, 10 H, i), 4.31–4.23 (m, 4 H, g), 3.98–3.93 (m, 2 H, F), 3.83–3.80 (m, 2 H, I), 3.74–3.68 (m, 2 H, I), 3.53–3.48 (m, 2 H, J), 3.38–3.19 (m, 4 H, L + K), 2.75–2.71 (m, 2 H, G) ppm. ^{13}C NMR ($CHCl_3$): δ = 170.32, 168.98, 165.39, 145.77, 151.75, 147.19, 146.13, 145.95, 145.51, 145.27, 145.18, 144.42, 142.98, 142.53, 142.04, 141.95, 141.76, 140.01, 136.41, 137.32, 136.03, 135.71, 129.01, 126.87, 128.40, 127.86, 125.20, 121.06, 72.27, 70.74, 70.12, 69.30, 68.71, 68.24, 58.33, 54.09, 44.06 ppm. MS (ES): calcd. for $C_{138}H_{76}Fe_2N_7O_{12}$ $[M + H]^+$ 2135.4; found 2135.3. IR: $\tilde{\nu}$ = 2930.3, 2854.1, 1728.9, 1644.0, 1603.5, 1581.3, 1513.8, 1462.7, 1376.9, 1264.1, 1123.3, 1089.6, 1021.1, 893.8, 821.5, 741.5, 704.8 cm^{-1}. UV/Vis (THF): λ_{max} = 256, 303, 325, 431, 705 nm.

Thread 12: Compound **10**[53] (1.36 g, 1.25 mmol) was stirred in a mixture of trifluoroacetic acid (20 mL) and DCM (20 mL) for 22 h. The solvent was evaporated under vacuum. EDC (0.272 g, 1.37 mmol), **11**[44] (0.336 g, 1.25 mmol) and HOBt (0.185 g, 1.370 mol) were added to a solution of the residue in chloroform (anhydrous, stabilised with amylenes, 50 mL) under argon. The solution was stirred at room temp. for 10 min. Then NEt_3 (3 mL) was added and the solution was stirred under argon for 18 h. The solvent was evaporated and the residue was subjected to chromatography ($CHCl_3$/MeOH, 99:1) to obtain the title compound (146 mg, 10%). ^{1}H NMR ($CHCl_3$): δ = 8.67 (br. s, 2 H, A), 7.77 (br. s, 2 H, B), 7.36–7.22 (m, 10 H, C), 6.57 (t, J = 5 Hz, 1 H, D), 6.54 (t, J = 5 Hz, 1 H, D), 5.19 (d, J = 10 Hz, 1 H, F), 5.17 (s, 1 H, G), 4.96 (s, 1 H, I), 4.30 (d, 1 H, J = 10 Hz, J), 4.05–3.95 (m, 2 H, K), 3.93 (d, J = 5 Hz, 2 H, L), 3.74–3.68 (m, 4 H, M), 3.57 (t, J = 5 Hz, 2 H, N), 3.34 (c, J = 5 Hz, 2 H, O), 3.38–3.32 (m, 1 H, P), 2.93–2.87 (m, 1 H, Q) ppm. ^{13}C NMR ($CHCl_3$): δ = 172.26, 168.38, 155.73, 153.54, 152.28, 151.90, 147.24, 147.21, 146.20, 146.11, 146.08, 146.06, 146.01, 145.87, 145.85, 154.51, 145.43, 145.40, 145.36, 145.27, 145.21, 145.17, 145.11, 145.09, 145.60, 144.42, 144.31, 144.21, 143.07, 142.93, 142.62, 142.52, 142.50, 142.46, 142.09, 142.06, 142.05, 142.00, 141.97, 141.91, 141.84, 141.72, 141.66, 141.59, 141.46, 140.15, 140.12, 139.84, 139.41, 138.96, 136.95, 136.19, 135.97, 135.42, 128.75, 128.72, 128.66, 128.45, 127.28, 127.15, 81.00, 74.42, 70.48, 70.40, 70.14, 69.63, 69.18, 67.59, 58.71, 52.18, 43.37, 39.33 ppm. MS (ES): calcd. for $C_{89}H_{34}N_4O_4$ $[M]^+$ 1222.2; found 1222.2. IR (NaCl): $\tilde{\nu}$ = 3302.5, 3057.6, 2920.7, 1653.7, 1597.7, 1540.8, 1492.6, 1450.21, 1415.5, 1354.7, 1263.1, 1177.3, 1119.5, 1031.73, 828.3, 734.7, 700.0 cm^{-1}. UV/Vis (DCM): λ_{max} = 256, 309, 325, 430, 703 nm.

Rotaxane 13: A solution of *p*-xylylenediamine (204 mg, 1.499 mmol) in chloroform (anhydrous, stabilised with amylenes,

40 mL) containing NEt_3 (0.217 mL, 3.000 mmol) and a separate solution of **5** (646 mg, 1.499 mmol) in chloroform (anhydrous, stabilised with amylenes, 40 mL) were added simultaneously over 4 h to a stirred solution of thread **12** (146 mg, 0.119 mmol) in $CHCl_3$ (anhydrous, stabilised with amylenes, 20 mL) under argon. After the addition, the reaction mixture was stirred for an additional 60 min at room temperature. The solution was filtered through Celite and concentrated to dryness. Rotaxane **13** (45 mg, 17%) was separated from the unreacted thread **12** by chromatography ($CHCl_3$/MeOH, 199:1) followed by reprecipitation ($CHCl_3$/hexane, ×3). ^{1}H NMR ($CHCl_3$): δ = 8.63 (br. s, 2 H, A), 8.33 (s, 2 H, a), 8.05 (s, 4 H, b), 7.95 (br. s, 2 H, B), 7.60–7.50 (m, 4 H, c), 7.38–7.19 (m, 11 H, C + E), 6.95 (s, 8 H, d), 5.71 (br. s, 1 H, D), 5.26 (s, 1 H, G), 5.09 (d, J = 10 Hz, 1 H, F), 4.99 (t, J = 2 Hz, 4 H, e) 4.56–4.53 (m, 4 H, f), 4.55 (t, J = 2 Hz, 4 H, g), 4.48 (s, 1 H, I), 4.35 (s, 10 H, i), 4.32–4.22 (m, 5 H, f + J), 3.95–3.83 (m, 2 H, K), 3.70–3.62 (m, 4 H, M), 3.48 (t, J = 5 Hz, 3 H, N), 3.27–3.15 (m, 3 H, O + P), 2.90–2.80 (m, 1 H, Q), 2.73–2.69 (m, 2 H, L) ppm. ^{13}C NMR ($CHCl_3$): δ = 172.41, 170.31, 169.06, 165.46, 155.44, 153.19, 151.81, 151.64, 151.27, 147.24, 147.19, 146.17, 146.11, 146.05, 146.01, 145.86, 145.80, 145.51, 145.43, 145.38, 145.29, 145.26, 145.18, 145.06, 144.56, 144.30, 144.15, 143.03, 142.92, 142.63, 142.52, 142.51, 142.42, 142.04, 141.97, 141.93, 141.88, 141.79, 141.62, 141.57, 141.54, 141.47, 140.11, 139.88, 139.32, 138.37, 137.16, 137.04, 136.08, 136.01, 135.65, 135.36, 129.02, 126.91, 128.82, 128.37, 127.82, 125.09, 121.22, 121.20, 80.30, 75.27, 72.28, 70.72, 70.51, 69.27, 69.10, 58.27, 52.15, 44.05, 42.30, 40.01 ppm. MS (MALDI-TOF): calcd. for $C_{144}H_{82}Fe_2N_3NaO_{12}$ $[M + Na]^+$ 2250.5; found 2250.4. IR (NaCl): $\tilde{\nu}$ = 3307.3, 3074.9, 3041.2, 2915.8, 2849.3, 1730.8, 1654.6, 1530.2, 1453.1, 1264.1, 1123.3, 1092.5, 1025.0, 930.49, 907.3, 822.5, 729.0, 695.2 cm^{-1}. UV/Vis (THF): λ_{max} = 255, 310, 322, 431, 702 nm.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of **2**–**5**, **7**, **9** and **12**–**14**.

Acknowledgments

This work was carried out with partial support of the University of Trieste, the Consorzio Interuniversitario Nazionale per la Scienza e la Tecnologia dei Materiali, the Ministero dell'Instruzione dell'Università e della Ricerca (PRIN 2006 project 200634372, and Firb project RBNE033KMA), the European Union (EU) (Networks "WONDERFULL" and "EMMMA") and the Freiburg Institute for Avanced Studies (Junior Fellowship).

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Received: November 16, 2009
Published Online: January 19, 2010

