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Synthesis and conformational analysis of redox-active ferrocenyl-calixarenes

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ABSTRACT

A novel synthetic approach toward redox-active calixarene-based receptors is described wherein ferrocene fragments have been introduced at the lower rim through anion-binding urea or amide connections. A thorough ^{1}H NMR investigation on a series of calixarene-ferrocene receptors was performed in order to estimate their hydrogen bonding-driven self-association properties and improve our understanding of the correlation between molecular structures and redox properties.

1. Introduction

Some 30 years after the pioneering work of Gutsche in the field of calixarene chemistry,[1] a great number of calixarene-based ligands have been engineered and studied for their versatile binding properties.[2] Their potential for cation extraction or sensing has especially prompted the development of numerous redox or photoactive calixarenes.[3] The accessibility of their lower and upper rims as well as the existence of functionalizable phenolic hydroxy groups on macrocylic frameworks have made these architectures increasingly attractive for chemists working in host–guest chemistry.[4] A major theme of contemporary calixarenes chemistry is the development and applications of biologically active derivatives.[5]

Metallocene containing calixarenes have already been studied essentially to sense or activate molecular level processes. Beer has been pioneer in making metallocene appended calixarenes for analytical purposes or to investigate electrochemical interactions between multi-redox architectures.[6] Kaifer and co-workers reported a redox controlled dissociation of a self-assembled dimer[7] whereas Beer took advantage of the receptor's electrochemical activity as a signal of a recognition event.[8] Among the most relevant examples of such derivatives, one finds an hetero ditopic ferrocene receptors containing two ethyl ester calix[4]arene units bridged by a ferrocene amide moiety[9] or a tetraferrocenyl-calixarene in which metallocenes have been directly introduced on the upper rim.[10]

We previously described the syntheses of artificial receptors associating calixarene as modular platform and ferrocene redox-active fragments. We pointed out their anion-binding properties and specific affinity for phosphate anions.[11] These molecules were, however, originally designed to promote interactions between multiple redox units held in proximity through tight hydrogen bound networks.[12] In our previous investigation, none of the reported 1,3-disubtituted calixarenes, linked to ferrocenes through urea- or amide-linkers, revealed significant and obvious redox interactions. Such electrochemical response is evidently related to the distance between redox centers, to the effect of electron transfer on these lengths, and to the overall dynamic behavior of the molecules in solution. Although electrochemical methods are perfectly suited to reveal the lack of unequivocal redox interactions, they provide, however, no structural and/or dynamic informations on the molecular objects.

In the present study, we report the syntheses and conformational analyses of similar artificial receptors associating calixarene as modular platform and ferrocene redox-active fragments. We therefore performed a thorough ^{1}H NMR investigation on a series of calixarene-ferrocene receptors to estimate their hydrogen bonding-driven self-association properties and improve our understanding of the correlation between molecular structures and redox properties.

2. Synthesis

The ferrocene propanoic acid **2**[13] (Scheme 1) was prepared from the ferrocene carboxaldehyde via a Horner–Wardsworth–Emmons olefination in quantitative yield. The last steps are the double bond hydrogenation followed by a saponification of the ester function to afford **2** in 78% yield.

The synthesis of the 1,3-bis(amino)-calix[4]arene was previously described in two steps from 4-*tert*-butylcalix[4]arene in

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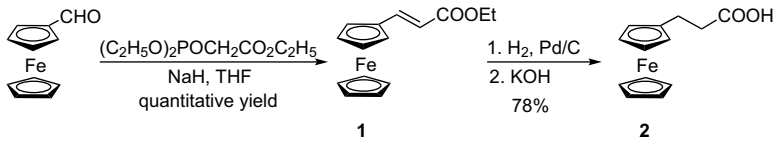
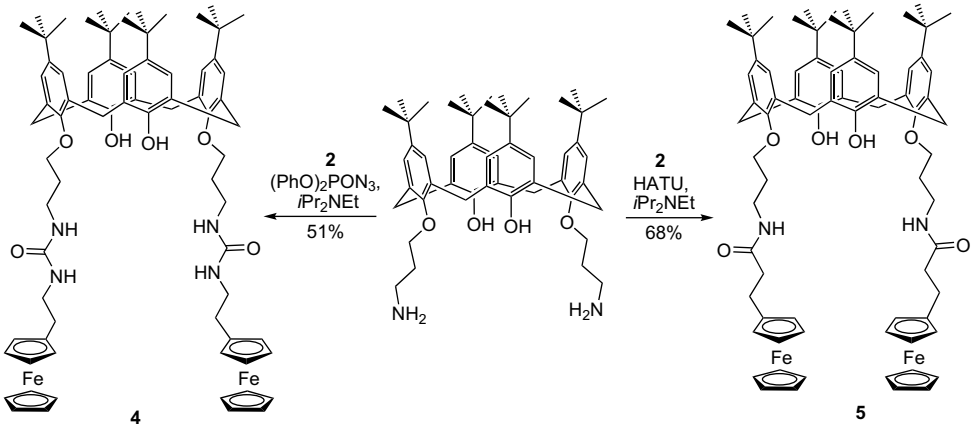


Scheme 1.

good yield.[14] From the 1,3-bis(amino)-calixarene and ferrocene propanoic acid, we synthesized compounds **4** and **5** in one step (Scheme 2) via a Curtius rearrangement and a peptide coupling method. This straightforward approach allowed us to readily isolate two derivatives using the same starting materials.

spectra of **4** (see Fig. 2) and **5** shows the expected splitting pattern for the methylene bridges, aromatic rings, and alkyl spacers, corresponding to C_{2v} symmetry of the calixarene ring. In the same way, ^{1}H NMR of compound **8** exhibit resonance signals corresponding to C_{4v} symmetry. Compounds **4** and **5** are present in symmetrical cone

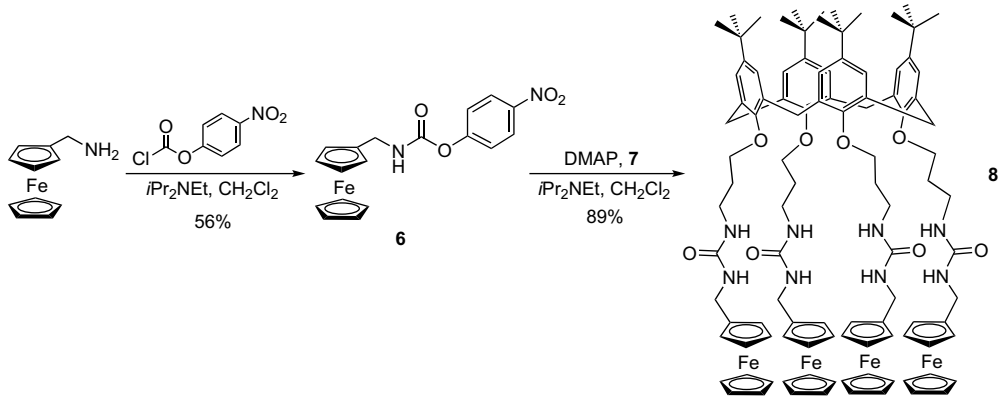


Scheme 2.

The tetraaminocalix[4]arene **7** in cone conformation, precursor of compound **8**, was prepared as described in the literature.[15] The aimed tetra-ureaferrocenyl derivative **8** could be obtained in relatively low yield (15%) through a Curtius rearrangement between **2** and a tetraaminocalix[4]arene precursor. This yield could, however, be improved up to nearly 90% using Paul Beer's strategy upon using **6** as ferrocene–urea precursor (Scheme 3).

conformation as proved by the low value of $\Delta\delta$ between the signals of the two sets of aromatic protons (respectively, $\Delta\delta$=0.016 and 0.01 ppm in DMSO-d_6) and *tert*-butyl groups (respectively, $\Delta\delta$=0.047 and 0.048 ppm in DMSO-d_6).

Information about the solvent accessibility of all NH protons in **4**, **5**, **8** and their level of engagement in H-bonding could be obtained from temperature coefficients. The relative change in



Scheme 3.

3. ^{1}H NMR studies

The structure of the synthesized compounds **4**, **5**, and **8** was proved by ^{1}H and ^{13}C NMR and mass spectroscopy. The ^{1}H NMR

chemical shifts recorded as temperature is changed by 1 K ($\Delta\delta/\Delta T$) is indeed an accurate probe to estimate the level of hydrogen bonding in molecular systems. The temperature dependence ($\Delta\delta/\Delta T$) of the ^{1}H NMR chemical shifts attributed to the NH signals in **4**,

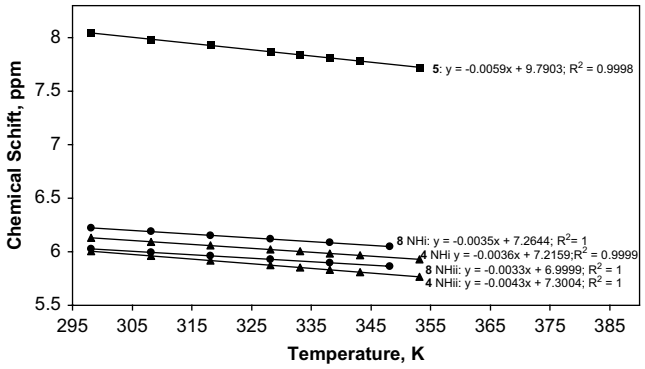


Figure 1. Dependence of the chemical shift of NH protons on the temperature.

5, and **8** was evaluated in DMSO-d_6 as already described in the literature.[16] In this polar and H-bond acceptor media, intermolecular hydrogen bonds and those established with solvent molecules are known to be readily cleaved by increasing temperature.[17,19] Upon increasing temperature in the range 298–353 K the signals of the NH groups are shifted up-field in a similar manner Figure 1.

A typical displacement observed with **4** between 298 and 353 K is depicted on Figure 2.

Moreover we known from literature that $\Delta\delta/\Delta T$ values found below −4.0 ppb/K for amide protons unambiguously reveal the absence of intramolecular hydrogen bonding processes.[19] Temperature coefficient was measured for **4**, **5**, and **8** upon recording several ^{1}H NMR spectra between 298 and 353 K. All of these analyses were performed on 3.0 mM solutions to assure the absence of significant molecular aggregation. All of the recorded and calculated results are summarized in Table 1.

From the low $\Delta\delta/\Delta T$ values calculated for the bis-amide derivative **5**, we readily inferred the absence of interactions between both amide arms. Surprisingly, both NH's of the urea-linked ferrocene-calixarene **4** turned out to exhibit significantly different $\Delta\delta/\Delta T$ values. Whereas NHs on the calixarene side (NH_i $\Delta\delta/\Delta T$=−3.6 ppm/K) are clearly involved in intramolecular H-bonding, lower value (NH_{ii} $\Delta\delta/\Delta T$=−4.4 ppm/K) calculated for NH's on the ferrocene side suggest simple solvent effects. The most positive $\Delta\delta/\Delta T$ values were found for the tetra urea-linked ferrocene-calixarene **8**. In contrast to what was found with **4**, both NH's in **8** exhibit similar values strongly suggesting the existence of an intramolecular hydrogen bonding network between all of the four urea groups. In view of these results, ROESY analysis was carried on for

Table 1
Spectroscopic data for compounds **4**, **5**, and **8**

Compounds	Protons	δ (ppm) at 298 K	$\Delta\delta/\Delta T$ (ppb/K)
4	NH_i[a]	6.13	−3.6
	NH_{ii}[b]	6.00	−4.4
5	NH	8.04	−5.9
8	NH_i[a]	6.22	−3.5
	NH_{ii}[b]	6.02	−3.3

[a] NH_i stands for NH's on the calixarene side.
[b] NH_{ii} stands for NH's on the ferrocene side (DMSO-d_6, 500 MHz).

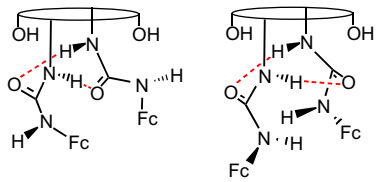


Figure 3.

compounds **4** and **8** to obtain more information. Selective irradiation of each NH for compound **8** revealed correlations between NH_i and O–*CH*$_2$–CH$_2$–*CH*$_2$, NH_{ii}, and between NH_{ii} and NH_i, *CH*$_2$–*HFc*. Concerning **4**, same type of correlation was observed for NH_i. However, NH_{ii} correlated only with NH_i. Based on these results, which suppose that only NH_i are engaged in a H-bonding, we assume that the urea was in *trans* configuration and/or the bottom part of the molecule was outside the cavity (Fig. 3).

4. Electrochemical analysis

The redox signatures of **4**, **5**, and **8** did not reveal strong interactions between ferrocenes, as proved by the observation of one single wave on their cyclic voltammograms corresponding to the simultaneous oxidation of all iron centers (Fig. 4). The weak 'interaction level' between redox moieties could nevertheless subtly be appraised upon measuring and comparing the difference between oxidation and reduction peak potentials (ΔE_p), assuming that hints of 'communication' between redox centers should bring about inequivalence signaled by larger ΔE_p values.

The experimental values reported in Table 2 are interestingly in full agreement with the outcomes of NMR spectroscopy establishing that **8** and **4** exhibit stronger intramolecular hydrogen bonding. Albeit numerous physico-chemical parameters might contribute to these deviation in electrochemical activities (number of redox centers, adsorption processes, kinetics…), the changes in ΔE_p and

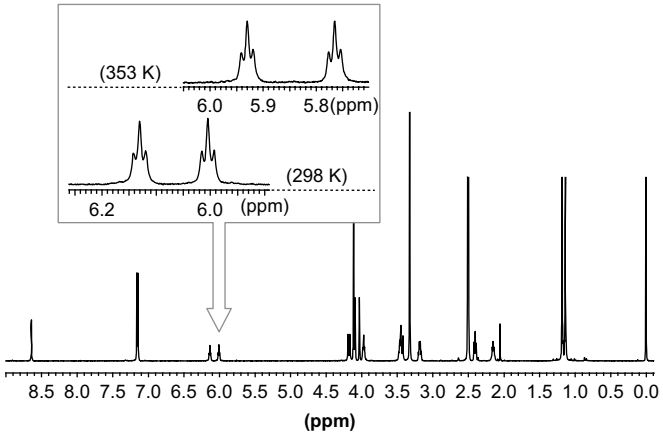


Figure 2. ^{1}H NMR spectrum of **4** (DMSO-d_6, 500 MHz, 298 K). Enlargement showing the effect of temperature on both NH of the urea's chemical shifts.

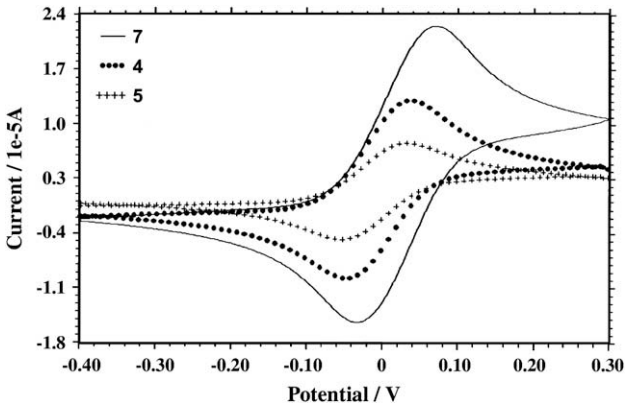


Figure 4. Cyclic voltammogram of **4**, **5**, and **7** in DMSO at 1×10^{-3} M on glassy carbon electrode (0.071 cm^2) of DMSO solution containing 0.1 M TBAP. Scan rate=100 mV/s.

Table 2
Electrochemical data recorded by cyclic voltammetry for **4**, **5**, and **8** dissolved in DMSO (0.1 M TBAP, vitreous carbon electrodes ∅=3 mm, 100 mV/s)

	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)	ΔE_p (mV)
4	38	−48	−5	86
5	26	−50	−12	76
8	66	−34	16	100

E_{pa} (anodic peak potential), E_{pc} (cathodic peak potential), $E_{1/2}=(E_{pa}+E_{pc})/2$; $\Delta Ep=E_{pa}-E_{pc}$.

$\Delta\delta/\Delta T$ values, calculated in DMSO for a series of structurally related receptors, are consistent and led to similar conclusions.

In conclusion, we have described the synthesis of original calix[4]arenes wherein ferrocene fragments have been introduced at the lower rim through urea or amide connections. We especially assessed the presence and/or the lack of intramolecular hydrogen bonds by NMR spectroscopy and correlated information with electrochemical analysis.

5. Experimental section

5.1. General

Starting materials and solvents were obtained from commercial suppliers and used without further purification. TLC: silica gel 60 F_{254}. NMR spectra were recorded on DRX 300 or DRX500 Brücker FT spectrometer. Abbreviation was used as: s (singlet), d (doublet), dd (divided doublet), t (triplet), q (quadruplet), m (multiplet) and l (large). Mass spectra were recorded by electrospray at the Mass Spectrometry centre. The synthesis of compound **6** [667886-34-2][10] was realized according to the literature procedure.

5.2. Synthesis of ethyl ferrocenylacrylate 1[18]

Triethyl phosphonoacetate (5.2 mL, 30 mmol) was added to a stirred suspension of sodium hydride (1.16 g, 31 mmol) in THF (50 mL) at 0 °C to give white foam. The mixture was allowed to warm to room temperature for 30 min, then cooled in an ice bath and compound **7** (5 g, 23.3 mmol) was added as a solution in THF (50 mL). After 20 min, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Saturated aqueous ammonium chloride was then added to the mixture. Diethyl ether was added and the combined layers were washed with water, dried ($MgSO_4$), and the solvent removed under vacuum. Purification by column chromatography (silica gel, dichloromethane) affords compound **8** in 98% yield (6.5 g). ^{1}H NMR (300 MHz, $CDCl_3$): 7.56 (d, J=15.8 Hz, 1H, CH), 6.03 (d, J=15.8 Hz, 1H, CH), 4.48 (m, 2H, HFc), 4.39 (m, 2H, HFc), 4.22 (q, J=7.2 Hz, 2H, CH_2), 4.15 (s, 5H, HFc), 1.32 (t, J=7.2 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 167.4, 145.7, 115.1, 78.8, 70.9, 69.7, 68.7, 60.3, 14.5.

5.3. Synthesis of ferrocenepropanoic acid 2

A solution of 1 g (3.52 mmol) of ethyl ferrocenylacrylate **1** and 0.10 g (1 mmol) of palladium-on-charcoal in 50 mL of ethanol was degassed under argon for 30 min before saturated with hydrogen. The mixture was vigorously stirred for 24 h. The filtration and the concentration under reduced pressure gave 1 g (95%) of yellow crystals corresponding to ethyl 3-ferrocenylpropanoate [162823-10-1].[19] ^{1}H NMR (300 MHz, $CDCl_3$): 4.31 (s, 9H, HFc), 2.45 (s, 4H, CH_2), 4.39 (q, 2H, J=7 Hz, CH_2), 1.21 (t, 3H, J=7 Hz, CH_3).

Potassium hydroxide (3.92 g, 70 mmol) in 10 mL of water was added to a solution of ethyl 3-ferrocenylpropanoate (2.0 g, 7 mmol) in ethanol (60 mL). After 8 h at reflux, the reaction mixture was concentrated in vacuo, then diluted with water and washed with diethyl ether. The aqueous phase was acidified with HCl 1 M and extracted with diethyl ether. The organic phase was dried over $MgSO_4$, filtered, and concentrated under vacuum. Ferrocenepropanoic acid **2** was obtained in 83% yield (1.5 g). ^{1}H NMR (300 MHz, $CDCl_3$): 11.03 (br s, 1H), 4.02–4.08 (m, 9H, HFc), 2.49–2.63 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 180.1, 87.6, 68.9, 68.3, 67.9, 67.0, 35.9, 25.0.

5.4. Procedure for Curtius rearrangement

Diisopropylethylamine (1.57 mL, 9 mmol) and diphenylphosphoryl azide (1.21 g, 4.4 mmol) were added to a solution of ferrocene propanoic acid (0.568 g, 2.2 mmol) dissolved in dry toluene (15 mL). The reaction mixture was heated at 70 °C for 2 h, then 5,11,17,23-tetra(*tert*-butyl)-25,27-bis(3-aminopropoxy)-26,28-dihydroxycalix[4]arene (0.734 g, 1 mmol) was added. After 2 h at 70 °C, the reaction mixture was concentrated under vacuum and purified by flash chromatography (silica gel, ethyl acetate–cyclohexane 6:4) to afford the desired product in 51% yield. Mp=159–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.87 (s, 2H, O*H*), 7.09 (s, 4H, Ar*H*), 6.91 (s, 4H, Ar*H*), 5.81 (br s, 2H, N*H*), 5.26 (br s, 2H, N*H*), 4.08–4.22 (m, 26H, ArCH_2Ar, *H*Fc, CH_2O), 3.64–3.70 (m, 4H, CH_2NH), 3.20–3.34 (m, 8H, ArCH_2Ar, CH_2NH), 2.39–2.42 (m, 4H, CH_2CH_2Fc), 2.14–2.19 (m, 4H, $CH_2CH_2CH_2$), 1.30 (s, 18H, *t*-Bu), 1.03 (s, 18H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): 159.4, 149.9, 149.7, 148.1, 143.2, 132.9, 128.2, 126.2, 125.8, 77.7, 75.7, 69.6, 69.1, 68.7, 68.2, 41.8, 38.8, 34.5, 34.3, 32.4, 32.0, 31.4, 30.7, 30.5. IR: KBr pellets, cm^{-1}: 3370, 2959, 2869, 1651. HRMS calculated for $C_{76}H_{97}Fe_2N_4O_6$: 1273.6112, found: 1273.612.

5.5. Amide synthesis

HATU (450 mg 1.2 mmol) and diisopropylethylamine (0.2 mL, 1.2 mmol) was added to a solution of ferrocenepropionic acid (309 mg, 1.2 mmol) in DMF (3 mL) and stirred for 15 min at 25 °C. This solution was then transferred to a suspension of 5,11,17,23-tetra (*tert*-butyl)-25,27-bis(3-aminopropoxy)-26,28-dihydroxycalix[4]arene (370 mg, 0.49 mmol) in DMF (5 mL) via a cannula. After 2 h, the reaction mixture was concentrated and purified by flash chromatography (silica gel cyclohexane–ethyl acetate 6:4) to afford the compound **5** in 68% yield (443 mg). Mp=223–225 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (s, 2H, O*H*), 7.10 (s, 4H, Ar*H*), 6.85 (s, 4H, Ar*H*), 3.96–4.17 (m, 26H, ArCH_2Ar, *H*Fc, CH_2O), 3.62–3.67 (m, 4H, CH_2NH), 3.34 (d, 4H, J=12.9 Hz, ArCH_2Ar), 2.61–2.69 (m, 4H, CH_2CO), 2.41–2.44 (m, 4H, CH_2Fc), 2.05–2.14 (m, 4H, $CH_2CH_2CH_2$), 1.29 (s, 18H, *t*-Bu), 0.98 (s, 18H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): 173.5, 150.4, 149.7, 147.7, 142.7, 132.8, 128.0, 126.1, 125.7, 88.3, 77.6, 74.4, 69.2, 68.7, 67.8, 38.7, 37.2, 34.4, 34.3, 32.3, 32.0, 31.4, 29.5, 26.2. IR: KBr pellets cm^{-1}: 3333, 2954, 2869, 1635. Elem. Anal. calculated: C, 73.42; H, 7.62; N, 2.25. Found: C, 73.19; H, 7.55; N, 2.13.

5.6. Tetra-ferrocene–urea functionalized calix[4]arene 8

Tetraaminocalix[4]arene derivative **7** (480 mg, 0.55 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of **6** (878 mg, 2.31 mmol), diisopropylethylamine (1.5 mL, excess) and DMAP (catalytic) in CH_2Cl_2 (20 mL) and the mixture was stirred for 24 h under argon. The reaction mixture was washed with sodium carbonate solution, then the organic fraction was dried over $MgSO_4$, filtered, and the solvent removed under vacuum. The residue was purified by column chromatography (silica gel, ethyl acetate). The desired product was obtained in 89% yield (0.916 g). Mp >300 °C. ^{1}H NMR (500 MHz, DMSO-d_6): 6.78 (s, 8H, Ar*H*), 6.22 (br s, 4H, N*H*), 6.02 (br s, 4H, N*H*), 4.27 (d, 4H, J=12.3 Hz, ArCH_2Ar), 4.13–4.16 (m, 24H, *H*Fc), 4.05–4.07 (m, 12H, *H*Fc), 3.95–3.97 (m, 8H, CH_2NH), 3.76–3.82 (m, 4H, CH_2O), 3.21–3.29 (m, 8H, CH_2NH), 3.11 (d, 4H, J=13.2 Hz, ArCH_2Ar), 2.08–2.11 (m, 8H, $CH_2CH_2CH_2$), 1.00 (s, 36H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): 159.0, 154.1, 144.5, 134.2, 125.5, 88.2, 73.8, 69.2, 68.3, 68.09, 39.6, 39.3, 37.5, 34.3, 32.0, 31.8, 31.2. IR: KBr

pellets, cm^{-1}: 3376, 2961, 2867, 1634. HRMS calculated for $C_{106}H_{137}Fe_4N_8O_8$: 1873.79516, found: 1873.79483.

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