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Water soluble ferrocenyl and polyferrocenyl compounds: synthesis and electrochemistry

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Abstract

The preparation and the electrochemical properties of different classes of water soluble ferrocenyl and multiferrocenyl compounds are described. Two strategies have been applied: (1) molecules with up to four redox units have been synthesized by quaternization of 2-(*N*,*N*-dimethylamino)ethylferrocene or 1,1′-bis(2-(*N*,*N*-dimethylamino)ethyl)ferrocene with different organic halides; (2) the synthesis of compounds with four and more redox moieties is based on the use of well established poly(propylene imine) dendrimers; the reductive amination of formyl ferrocene with the NH_2-functions of these macromolecules leads to ferrocenyl dendrimers with a maximum of 64 metallocene units. The multi ammonium salts of these compounds exhibit solubility only in polar solvents. All prepared ferrocenes have been studied with voltammetric, amperometric and coulometric techniques.

Keywords: Electrochemistry; Ferrocenyl compounds; Dendrimers; Water solubility

1. Introduction

In recent years many groups have focused their research interests on the synthesis and electrochemical investigation of redox active compounds useful for electrochemical applications. For example, ferrocenyl and multiferrocenyl systems have been used as redox sensors for molecular recognition [1], as mediators in amperometric biosensors [2], as building blocks in polymers [3] or as coatings to modify electrode surfaces [4]. Most of the known compounds are only soluble in hydrophobic media, only few ferrocenyl and polyferrocenyl systems are water soluble [5]; such species are of particular interest as redox mediators, for example in scanning electrochemical microscopy (SECM) [6] investigations in biological systems. Here we report on the preparation and on the electrochemical properties of two different classes of ammonium compounds containing ferrocenyl systems. The synthesis of the class I compounds **3**–**10** with rather low molar weight is based on the quaternization of two dimethylaminoethyl substituted ferrocenes with several organic bromides; this reaction leads to molecules with up to four redox moieties. The class II compounds **13b**–**17b** with higher molar weight are prepared by functionalization of poly(propylene imine) dendrimers [7] with appropriately substituted ferrocenes; this strategy leads to molecules with up to 64 redox moieties. Voltammetric, coulometric and amperometric techniques have been applied to characterize the different ferrocenyl compounds.

2. Results

2.1. Synthesis

2-(*N*,*N*-Dimethylamino)ethylferrocene (**1**) [8] or 1,1′-bis(2-(*N*,*N*-dimethylamino)ethyl)ferrocene (**2**) [9] (Scheme 1) were used as starting material for the synthesis of the ferrocenyl ammonium salts **3**, **4**, **5**, **6** and **7**. Treatment of solutions of the benzylic bromides based on toluene, xylene, mesitylene and durene with ferrocenes **1** or **2** led to orange reaction mixtures which turned turbid soon after the addition due to the formation of the products.

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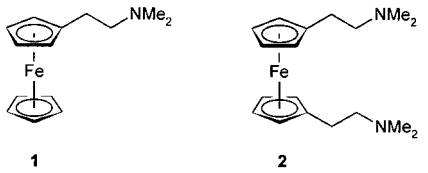


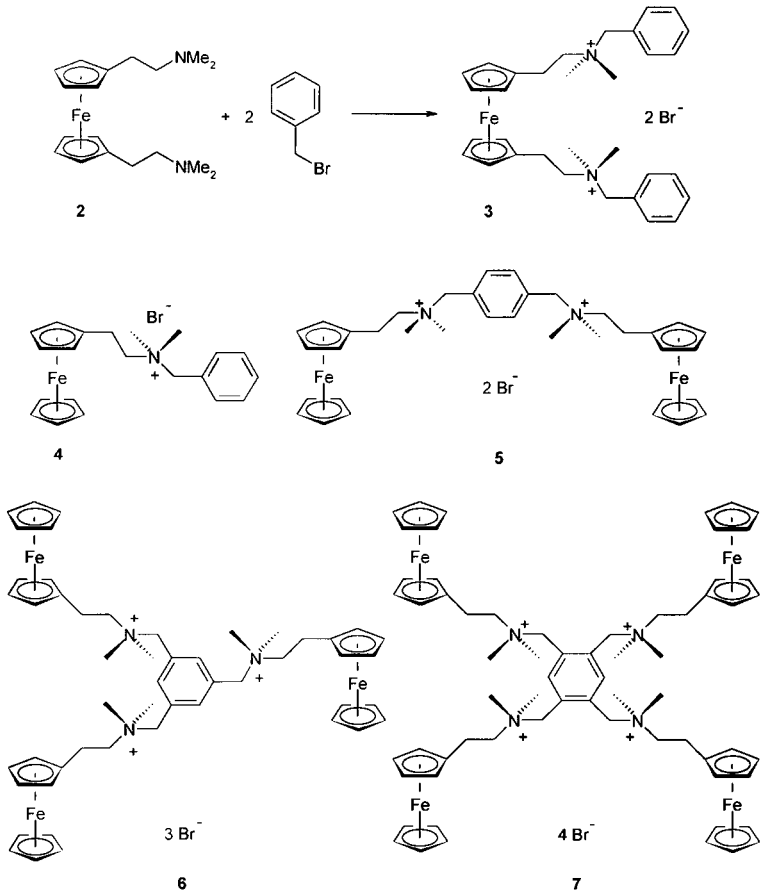
Scheme 1.

Compounds **3**–**7** (Scheme 2) could be obtained as slightly hygroscopic bright yellow solids which are only soluble in polar solvents like EtOH, DMSO and water. However, the solubility of these compounds decreases with their molar weight. In the ^{1}H-NMR spectra of compounds **3**–**7** the signals for the protons are generally shifted to lower field compared to those of the parent ferrocenes **1** and **2** due to the presence of the positively charged ammonium groups. The lowfield shift also depends on the number of positive charges per molecule. In general, an increase of positive charges causes an increase of the proton shift to lower field. Especially the values for the aromatic protons which increase in the sequence **4**→**5**→**6**→**7** from 7.53 to 8.27 exhibit this effect. In Table 1 the proton shifts of **4**–**7** (which are all based on ferrocene **1**) are given. The increasing number of charges also has an influence on the redox potentials of the ferrocenyl systems (see Section 2.2).

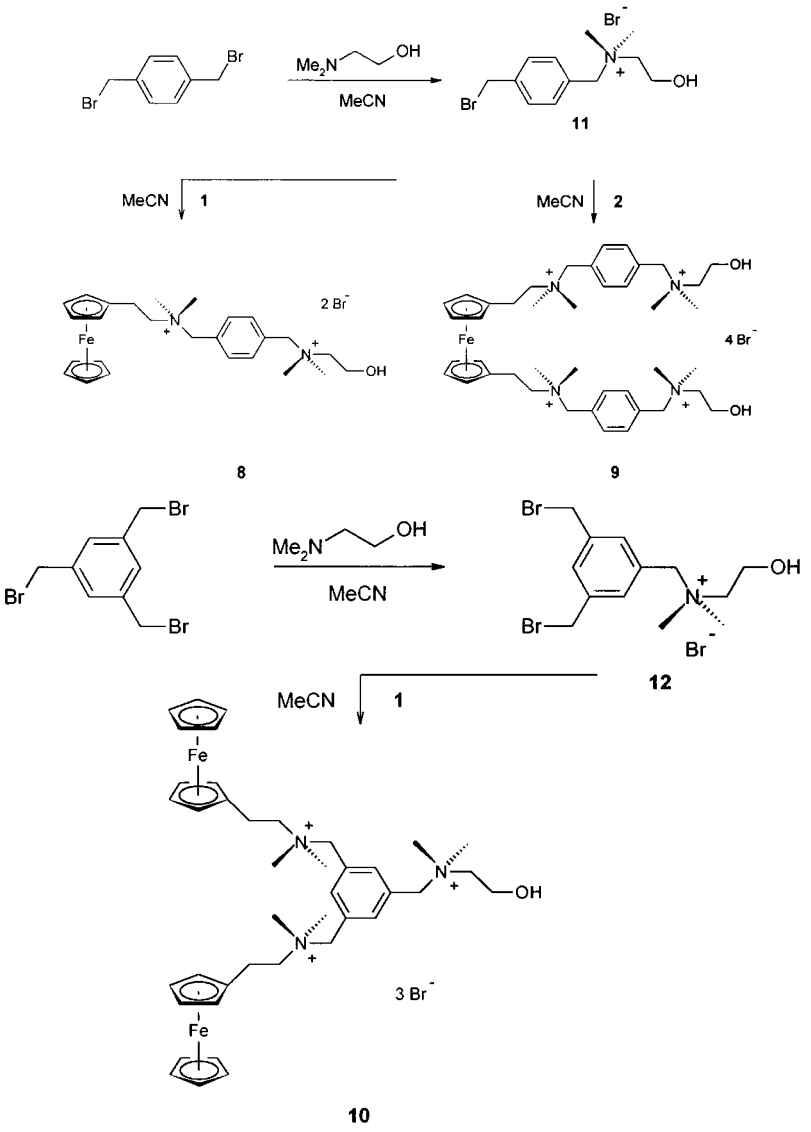
Table 1
^{1}H-NMR data of compounds **4**–**7** in DMSO-d_6; shifts in ppm

	Compound			
	4 (Fc^{Bz})	**5** (Fc^2)	**6** (Fc^3)	**7** (Fc^4)
Number of redox units	1	2	3	4
NCH_3	3.04	3.05	3.10	3.12
NCH_2CH_2	3.45	3.47	3.54	3.97
NCH_2CH_2	2.83	2.85	2.89	2.90
Cp–*H*	4.13–4.17	4.14–4.18	4.14–4.24	4.16–4.28
CH_2–benzyl	4.64	4.68	4.67	5.12
C*H*–phenyl	7.53–7.59	7.73	7.89	8.27

To improve the solubility of this kind of ferrocenyl systems we introduced additionally to the NR_4^+ group another hydrophilic function. The mixed ammonium salts **8**, **9** and **10** (Scheme 3) could be prepared in a two step synthesis. First the reaction of 2-(*N*,*N*-dimethylamino)ethanol with only one CH_2Br function of 1,4-bis(bromomethyl)benzene or 1,3,5-tris(bromomethyl)-benzene led to the mono ammonium compounds **11** and **12** in acceptable yields. Compounds **11** and **12**



Scheme 2. Synthesis of **3**, images of compounds **4**, **5**, **6** and **7**.



Scheme 3. Synthesis of **8**, **9** and **10**.

possess one OH-function in addition to the NR_4^+ group; one (**11**) or two (**12**) CH_2Br functions are still left for the second synthetic step, the linkage with the redox moieties of **1** and **2**. Compounds **8**, **9** and **10** could be obtained in good yields as slightly hygroscopic yellow solids which exhibit excellent solubility in EtOH, DMSO and water.

The preparation of multiferrocenyl compounds with up to 64 redox centers is based on the reductive amination of formyl ferrocene with different poly(propylene imine) dendrimers. In the first step the amino functions of the dendrimer were condensed with the aldehyde in toluene solution. The subsequent reduction of the formed imino groups with $NaBH_4$ in EtOH led to compounds with 4 (**13a**), 8 (**14a**), 16 (**15a**), 32 (**16a**), or 64 (**17a**) ferrocene moieties per molecule. The amino systems could be obtained as red waxy solids in good yields which are only soluble in organic solvents such as CH_2Cl_2, $CHCl_3$ and toluene. The quaternization of all NR_3 and NR_2H fragments in these molecules with HCl gas causes a drastic change in solubility from non polar to polar solvents. The substituted ammonium ferrocenyl systems **13b**–**17b** could be isolated as bright yellow solids which are only soluble in solvents like DMSO, EtOH and water. The larger systems with 32 and 64 redox moieties per molecule exhibit only poor solubility in DMSO or DMSO + water mixtures. Scheme 4 presents the synthesis of the tetraferrocenyl compound and a representation of the multiferrocenyl systems with 8, 16, 32 and 64 redox units per molecule.

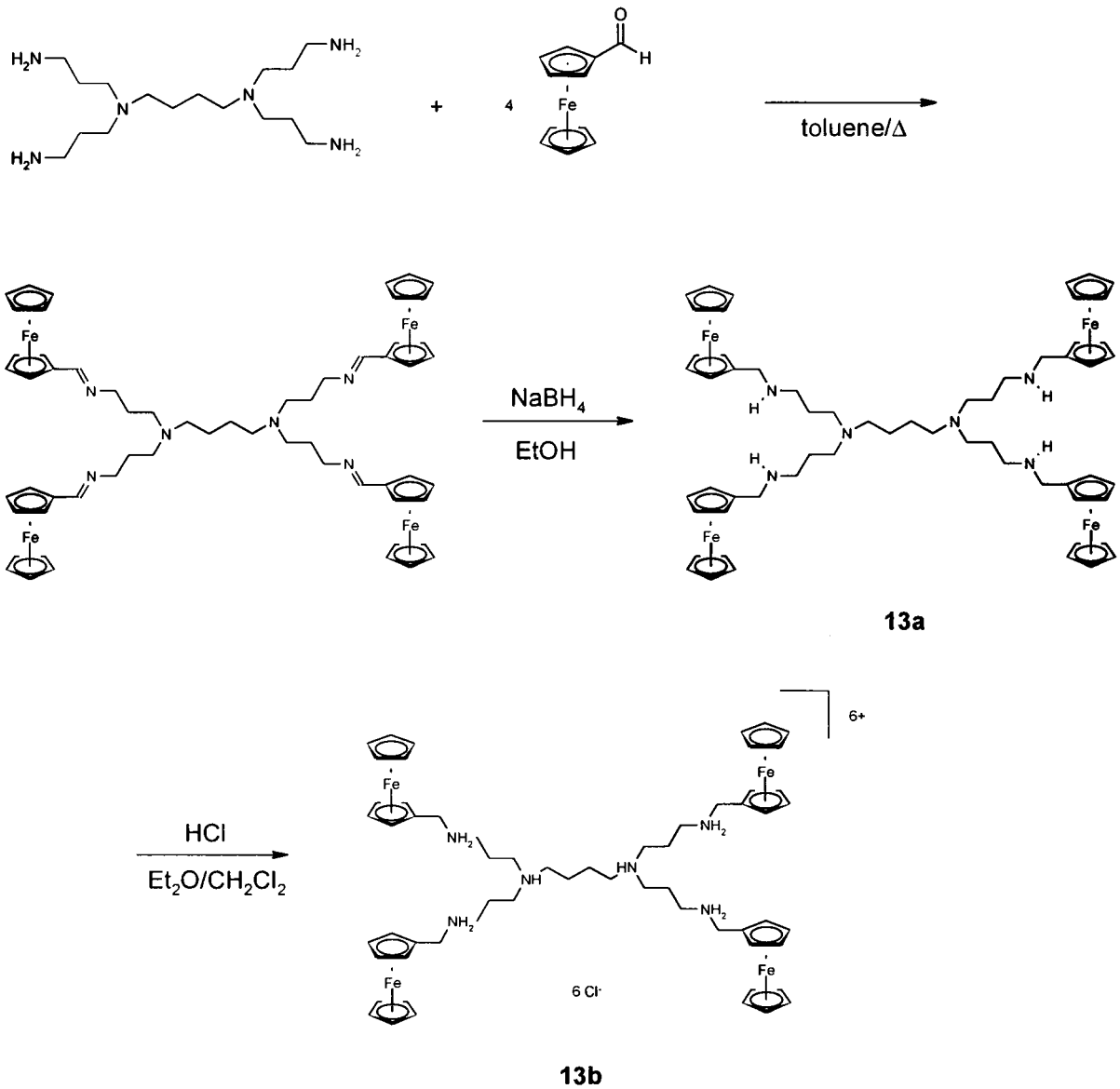
All compounds have been characterized by ^{1}H- and ^{13}C-NMR spectroscopy and by mass spectrometry (MALDI TOF). For the smaller systems with up to eight redox units an exact assignment of the proton and carbon shifts to the inner and outer methylene groups is

possible. In the spectra of the larger compounds the different signals of the dendritic methylene groups are no longer distinguishable. Only the signals of the respectve ferrocene units and of their α methylene groups could be separated and appear in the expected region. The NH_2^+ and NH^+ groups in **13b**–**17b** are revealed by signals at 9.4 and 11.1 ppm, respectively. The ratio of the integrals for the NH_2^+ and for the NH^+ resonance is nearly two to one due to a complete protonation of all inner and outer amino functions of **13a**–**17a**. In mass spectrometric investigations the amino and the corresponding ammonium systems show the same m/z peaks in form of the deprotonated species; this can be explained by the loss of HCl during vaporization from the MALDI matrix. All the collected NMR spectroscopic and mass spectrometric data reveal that the functionalization of the dendrimer with redox moieties is rather complete. Only the mass spectra of the large systems (**16a**,**b** and **17a**,**b**) indicate that the dendrimer periphery is not perfectly covered with ferrocene units.

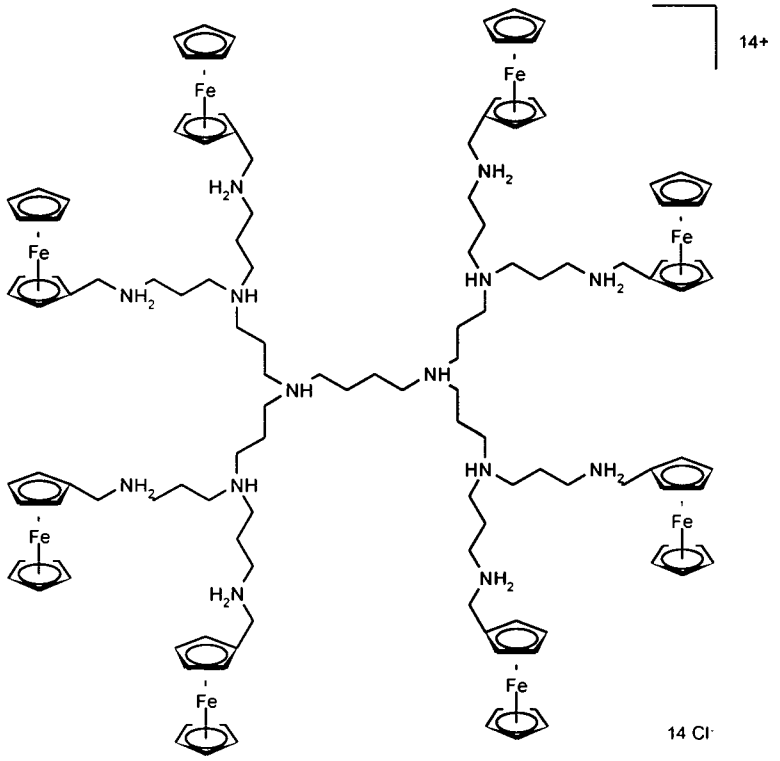
2.2. Voltammetric experiments

We examined the compounds **1**–**10** and **13a(b)**–**17a(b)** by cyclovoltammetry and square wave voltammetry and compared their electrochemical data. In Table 2 the $E_{1/2}$ values (vs. fc/fc^+) of the ammonium compounds in DMSO + 0.1 M TBAPF are summarized.

In **1**–**10** the reversibility of the redox processes is indicated by the fact that the observed peak separations of all cyclic voltammograms were comparable to the



Scheme 4. Synthesis of **13b**, images of **14b**, **15b**, **16b** and **17b**.



14b

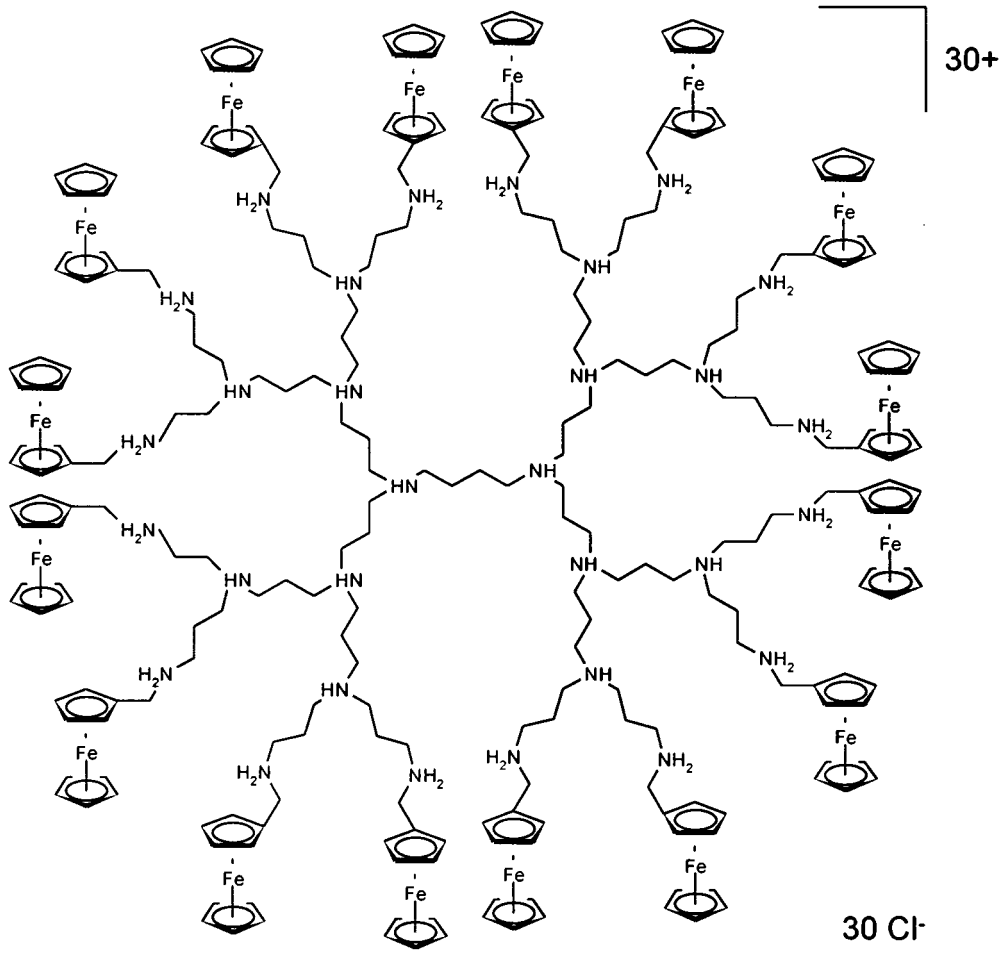
Scheme 4. (*Continued*)

ΔE_p values of decamethylferrocene which was used as internal reference. The E_ω values of the square wave voltammograms confirm the reversibility. All ferrocenyl ammonium compounds are more difficult to oxidize than ferrocene. The anodic shift towards the parent ferrocenes **1** and **2** are 170 mV (**3** and **9**) and 60 to 80 mV (**4**–**7**, **8** and **10**), respectively. This behavior can be explained by the different substitution pattern of the redox moieties of **3**–**10**. The two positively charged ammonium functions in **3** and **9** cause a larger anodic shift of the $E_{1/2}$ value than the only one function in the other compounds. For the compounds **4**–**7** the increasing number of positive charges per molecule also slightly influences the redox potential. The anodic shift of $E_{1/2}$ in the sequence **4**→**5**→**6**→**7** amounts to 20 mV.

In voltammetric measurements the multiferrocenyl compounds **13a(b)** to **17a(b)** show only one redox signal for a multi electron transfer. No interactions between the redox moieties can be observed. The redox potential of the ferrocenyl amines **13a** to **17a** amounts to 10–50 mV (in CH_2Cl_2 vs. fc/fc$^+$). Compared to the poly(propylene imine) dendrimers of Cuadrado and Morán [10] with a half-wave potential of 570–590 mV (in CH_2Cl_2 vs. SCE; equals 110–130 mV vs. fc/fc$^+$ [11]) the values of **13a** to **17a** are cathodically shifted (the potential difference amounts to 80–100 mV). The molecules also adsorb onto the working electrode surface during the electrochemical experiment. The potentials of the corresponding ammonium salts **13b**–**17b** amount to 90 mV each (in DMSO vs. fc/fc$^+$). In comparison with the ferrocenyl systems above, the half wave potentials are anodically shifted due to a shorter bridge between the positively charged ammonium group and the redox center ($-CH_2-$ instead of $-CH_2CH_2-$). Adsorption phenomena could not be observed.

2.3. Coulometric and amperometric experiments

The diffusion coefficients D for the ammonium compounds were measured by coulometric and amperometric experiments in DMSO solution relatively to ferrocene as standard. The obtained D values and the determined hydrodynamic radii (Stokes radii [12]) represent the average of several measurements; the values are listed in Table 3. Fig. 1 shows the diffusion coefficients as a function of the molar weight of the respective ferrocenyl system. As expected the D values decrease with increase of the molar weight M, an adaption of the parameters gives the following correlation: $D \sim M^{-0.67}$. Similar correlations have been found for macromolecular systems like ferrocenyl polymers as well as proteins [13].



15b

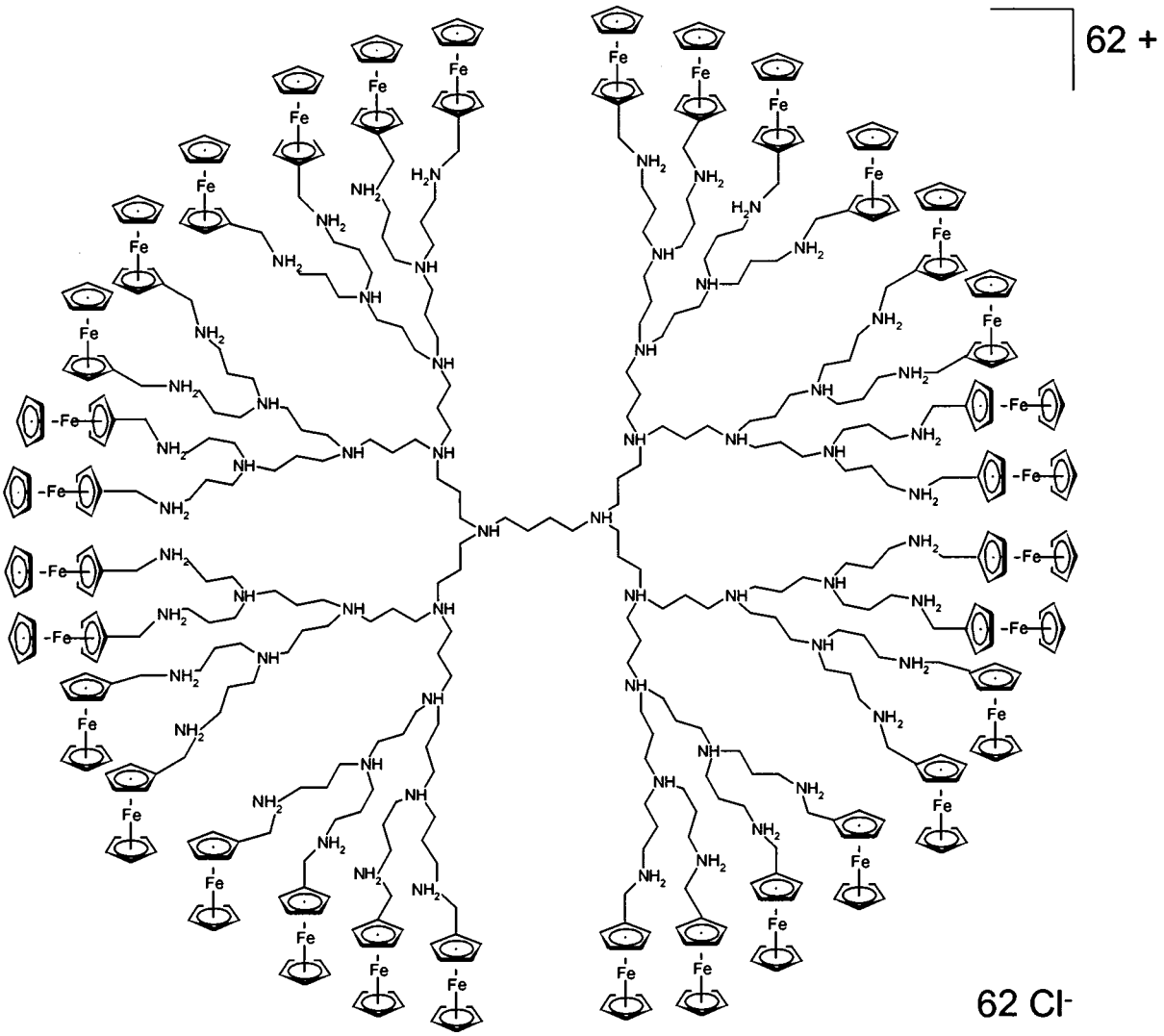
Scheme 4. (*Continued*)

The hydrodynamic radii give an impression of the dimension of the synthesized compounds in solution where they are surrounded by a solvating envelope. These values are calculated as Stokes radii for ball shaped molecules. A computer simulation (molecular mechanics MM+) of poly(propylene imine) dendrimers [15] shows that these macromolecules (especially the dendrimers of the fourth and fifth generation) have the shape of a 'drop' or of an ellipse [16] where the peripheric functions represent the surface of the molecule; the inner butylene unit of the dendrimer is situated in a cavity (the thinnest part of the 'drop'). The hydrodynamic radius for the largest synthesized system (**17b**) amounts to 47 Å (Stokes radius). This value is large compared to the corresponding MM+ modeled system which has a maximal diameter of 27 Å. The difference between these two values indicates that **17b** is surrounded by a bulky solvating envelope in DMSO solution; this behavior is not unusual for polar compounds dissolved in polar solvents.

For the dendritic multiferrocenyl systems **13b** to **17b** an expected increase of the hydrodynamic radii is observed. The increase amounts to 9.0–9.5 Å per generation. A linear dependence of these parameters as presented in Fig. 2 is typical of dendritic systems [16].

3. Conclusion

The preparation of two classes of hydrophilic ferrocenyl and multiferrocenyl ammonium compounds has been described. The first class includes systems with up to four redox units per molecule. Their synthesis is based on the quaternization of the amino ferrocenes **1** and **2** with different organic halides. This reaction type offers also the access to mixed quaternary systems which have an additional hydrophilic function (OH group). All products **3**–**10**, especially the compounds with hydroxy groups (**8**–**10**), show the desired solubility in polar solvents. Multiferrocenyl compound with up to



16b

Scheme 4. (*Continued*)

64 redox units (class II) have been prepared by functionalization of poly(propylene imine) dendrimers. The reductive amination of formyl ferrocene with these polyamino compounds and subsequent protonation with HCl leads to the polyammonium systems **13b**–**17b**.

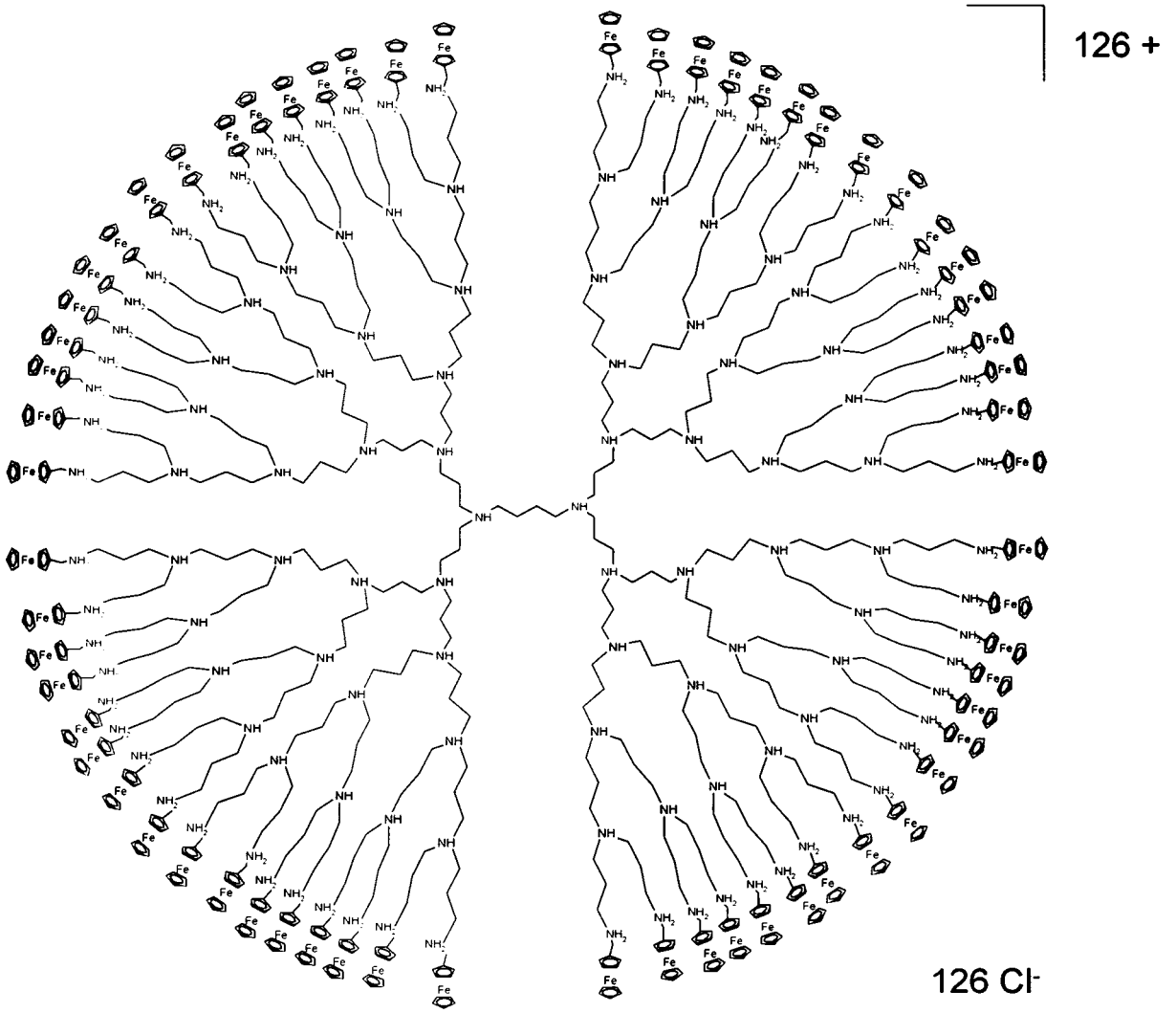
Voltammetric investigations of the ferrocenyl systems show that the redox potential depends on the length of the carbon bridge between redox centre and the respective ammonium group. For the compounds based on amino ferrocene **1** (**4**–**7**) $E_{1/2}$ values from 40 to 60 mV are obtained. The values for **3** and **9** (both based on ferrocene **2**) with two positive charges near the redox centre amount to 80 mV. For the multiferrocenyl compounds **13b**–**17b** the redox potentials amount to 90 mV (all vs. fc/fc^+).

The diffusion coefficients of the ferrocenyl systems could be determined by chronocoulometry and chronoamperometry in DMSO solution. The obtained values are a function of the molar weight of the molecules and allow the calculation of the hydrodynamic radii. For the dendritic systems **13b**–**17b** a linear correlation between the radius and the number of generations could be observed.

4. Experimental

4.1. General

All experiments were carried out under argon. Solvents were dried and purified by distillation. Commer-



17b

Scheme 4. (*Continued*)

cially available starting materials were used without further purification. Poly(propylene imine) dendrimers were purchased from Aldrich. 1,1′-bis(2-(*N*,*N*-dimethylamino)ethyl)ferrocene (**2**) [9], 1-chloro-2-*N*,*N*-dimethylaminoethane [8], $Fe(C_5H_5)(C_5H_4Li)$ [17], 1,3,5-tris(bromomethyl)benzene and 1,2,4,5-tetrakis-(bromomethyl)benzene [18] were prepared as described. NMR measurements: Bruker Avance DRX 500 (^{1}H-NMR: 500.1 MHz; $^{13}C\{^1H\}$-NMR: 125.8 MHz). Chemical shifts are given relative to $SiMe_4$. Mass spectra: PE Biosystems Voyager System 1161, MALDI-TOF with dihydroxy benzoic acid (DHB) as matrix. Only characteristic m/z values are listed. Compounds **15b**–**17b** tend to include solvent molecules in the dendritic cavities, as detected by ^{1}H-NMR spectroscopy [10a].

4.2. Electrochemistry

The electrochemical experiments were performed with a EG&G PARC Model 273A potentiostat/galvanostat in combination with the Model 270 software. A three-electrode configuration was employed. The working electrode was a platinum disc (diameter 2 mm). The counter electrode was a platinum wire. A silver wire was used as pseudo reference electrode. The potentials were referenced to that of decamethylferrocene as the internal reference [19]. DMSO (commercially available) or CH_2Cl_2 (each containing 0.1 M NBu_4PF_6 (TBAPF) as the supporting electrolyte) was used as the solvent for the measurements. All potentials were determined by cyclovoltammetry (scan rate 100 mV s^{-1}) and square-wave voltammetry (frequency 5

Table 2
Redox potentials $E_{1/2}$ of compounds **1**–**10** and **13b**–**17b**; in DMSO + 0.1 M TBAPF relative to ferrocene/ferrocenium

Compound	Number of redox units	$E_{1/2}$ (vs. fc/fc$^+$) (mV)
1	1	−20
4 (Fc^{Bz})	1	40
5 (Fc^{2})	2	40
6 (Fc^{3})	3	50
7 (Fc^{4})	4	60
8 (Fc^{OH})	1	40
10 ($2Fc^{OH}$)	2	40
2	1	−90
3 (Fc^{2Bz})	1	80
9 (Fc^{2OH})	1	80
13b (DAB–Fc-4 × 6HCl)	4	90
14b (DAB–Fc-8 × 14HCl)	8	90
15b (DAB–Fc-16 × 30HCl)	16	90
16b (DAB–Fc-32 × 62HCl)	32	90
17b (DAB–Fc-64 × 126HCl)	64	90

Hz). The diffusion coefficients D were determined by chronocoulometry and chronoamperometry as double step experiment relative to the value of ferrocene (6.50×10^{-6} cm^2 s^{-1} [20]).

4.3. Synthesis of 2-(*N*,*N*-dimethylamino)ethylferrocene (*1*)

A solution of 1.0 g (9.8 mmol) 1-chloro-2-*N*,*N*-dimethylaminoethane in 15 ml THF was added slowly to a stirred suspension of $Fe(C_5H_5)(C_5H_4Li)$ in 40 ml THF at room temperature (r.t.). After the addition the mixture is stirred for 14 h. The solvent is removed in vacuo and the residue is suspended in 50 ml petroleum ether and filtered. The solution is treated with 50 ml diluted HCl. The aqueous layer is separated and treated with 50 ml CH_2Cl_2. To the stirred mixture concentrated KOH solution is added dropwise till the color of the organic layer turns red. The organic layer is separated, washed twice with 50 ml water and dried over Na_2SO_4. After removing the solvent **1** can obtained as red oil. Yield: 42% (1.02 g, 4.0 mmol). ^{1}H-NMR ($CDCl_3$): $\delta = 2.25$ (s, 6H, CH_3); 2.43 (m, 2H, CpCH_2); 2.48 (m, 2H, CH_2N); 4.03 (s, 2H, Cp*H*); 4.07 (s, 2H, Cp*H*); 4.08 (s, 5H, Cp*H*). $E_{1/2} = -20$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). See also [8].

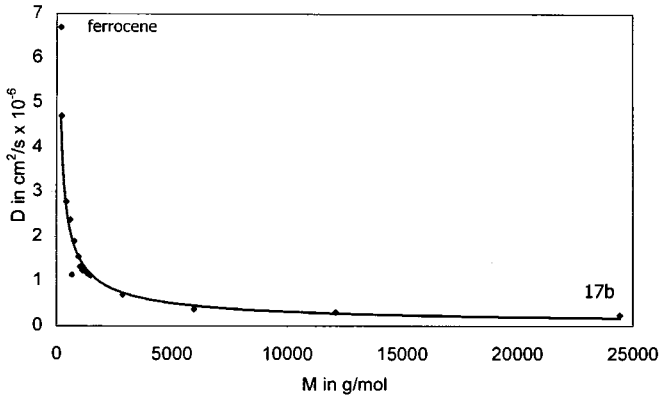


Fig. 1. Plot of diffusion coefficients D versus molar weight M of the compounds given in Table 3.

4.4. Synthesis of *3* (Fc^{2Bz})

Bromomethylbenzene (2.8 g, 16.4 mmol) are added to a solution of 0.47 g (1.43 mmol) 1,1′-bis(2-(*N*,*N*-dimethylamino)ethyl)ferrocene in 20 ml hexane at r.t. After the addition the orange solution turns turbid. The mixture is stirred for 14 h. The solvent is removed in vacuo and the residue is washed twice with 15 ml hexane. Compound **3** can be obtained as yellow solid. Yield: 85% (0.82 g, 1.22 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.87$ (m, 4H, CpCH_2CH_2N); 3.06 (s, 12H, CH_3)

Table 3
Diffusion coefficients D and hydrodynamic radii r_{hyd} of compounds **3**–**10**, **13b**–**17b**, ferrocene and acetyl ferrocene

Compound	Molar weight (g mol^{-1})	Diffusion coefficient D (cm^2 s^{-1} × 10^{-6})	Hydrodynamic radius r_{hyd} (Å)
Ferrocene	186.04	6.70	1.7
Acetyl ferrocene	228.07	4.71 [14]	2.3
4 (Fc^{Bz})	428.19	2.78	4.0
8 (Fc^{OH})	610.25	2.38	4.6
3 (Fc^{2Bz})	670.35	1.13	9.7
5 (Fc^{2})	778.26	1.89	5.8
10 ($2Fc^{OH}$)	960.32	1.54	7.1
9 (Fc^{2OH})	1034.47	1.31	8.4
6 (Fc^{3})	1128.33	1.23	9.0
13b (DAB–Fc-4 × 6HCl)	1327.48	1.17	9.4
7 (Fc^{4})	1478.40	1.12	9.9
14b (DAB–Fc-8 × 14HCl)	2868.11	0.69	15.9
15b (DAB–Fc-16 × 30HCl)	5949.19	0.37	29.6
16b (DAB–Fc-32 × 62HCl)	12111.53	0.31	36.0
17b (DAB–Fc-64 × 126HCl)	24436.19	0.24	46.6

3.50 (m, 4H, $CpCH_2CH_2N$) 4.13 (s, 2H, Cp*H*); 4.21 (s, 2H, Cp*H*); 4.69 (s, 4H, CH_2Ph); 7.53 (m, 6H, Ph*H*); 7.61 (m, 4H, Ph*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 21.9$ ($CpCH_2CH_2N$); 49.1 (CH_3); 63.5 (CH_2Ph); 66.2 ($CpCH_2CH_2N$); 68.5, 68.7, 83.2 (Cp–*C*); 128.2, 128.9, 130.3, 133.0 (Ph–*C*). Anal. Calc. for $C_{32}H_{42}N_2Br_2Fe \times 0.5H_2O$: (679.37 g mol^{-1}): C, 56.49; H, 6.52; N, 4.12 [21]. Found: C, 56.82; H, 6.51; N, 3.92%. $E_{1/2} = 80$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 1.13 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.5. Synthesis of **4** (Fc^{Bz})

The preparation of **4** is similar to that of **3** above (2.9 g (17.0 mmol) bromomethylbenzene, 0.18 g (0.70 mmol) 2-(*N*,*N*-dimethylamino)ethylferrocene in 20 ml CH_2Cl_2). Yellow solid. Yield: 83% (0.25 g, 0.58 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.83$ (m, 2H, $CpCH_2CH_2N$); 3.04 (s, 6H, CH_3); 3.45 (m, 2H, $CpCH_2CH_2N$); 4.13 (s 2H, Cp*H*); 4.16 (s, 5H, Cp*H*); 4.17 (s, 2H, Cp*H*); 4.64 (s, 2H, CH_2Ph); 7.53 (m, 3H, Ph*H*); 7.59 (m, 2H, Ph*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 21.9$ ($CpCH_2CH_2N$); 49.1 (CH_3); 63.3 (CH_2Ph); 66.4 ($CpCH_2CH_2N$); 67.5, 67.8, 68.5, 82.8 (Cp–*C*); 128.1, 130.0, 130.3, 133.0 (Ph–*C*). Anal. Calc. for $C_{21}H_{26}NBrFe \times 0.75H_2O$ (441.71 g mol^{-1}): C, 57.10; H, 6.28; N, 3.17 [21]. Found: C, 57.10; H, 6.23; N, 3.46%. $E_{1/2} = 40$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 2.78 \times 10^{-6}$ cm^2 s^{-1} (DMSO/0.1 M TBAPF).

4.6. Synthesis of **5** (Fc^2)

2-(*N*,*N*-Dimethylamino)ethylferrocene (0.32 g, 1.24 mmol) was added to a solution of 0.16 g (0.61 mmol) 1,4-bis(bromomethyl)benzene in 25 ml MeCN at r.t. After the addition the orange solution turns turbid. The mixture was stirred for 14 h. The solvent was removed in vacuo and the residue was washed twice with 20 ml hexane. Compound **5** can be obtained as yellow solid. Yield: 95% (0.45 g, 0.58 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.85$ (m, 4H, $CpCH_2CH_2N$); 3.05 (s, 12H, CH_3); 3.47 (m, 4H, $CpCH_2CH_2N$); 4.14 (s, 4H, Cp*H*); 4.18 (s, 14H, Cp*H*); 4.68 (s, 4H, CH_2Ph); 7.73 (s, 4H, Ph*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 21.9$ ($CpCH_2CH_2N$); 49.2 (CH_3); 63.5 (CH_2Ph); 65.6 ($CpCH_2CH_2N$); 67.5, 67.9, 68.5, 82.8 (Cp–*C*); 130.1, 133.4 (Ph–*C*). Anal. Calc. for $C_{36}H_{46}N_2Br_2Fe_2$ (778.26 g mol^{-1}): C, 55.56; H, 5.95; N, 3.60. Found: C, 55.41; H, 6.04; N, 3.63%. $E_{1/2} = 40$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 1.89 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.7. Synthesis of **6** (Fc^3)

The preparation of **6** is similar to that of **5** above (0.44 g (1.71 mmol) 2-(*N*,*N*-dimethylamino)ethylferrocene, 0.2 g (0.56 mmol) 1,3,5-tris(bromomethyl)benzene in 15 ml MeCN). Yellow solid. Yield: 83% (0.47 g, 0.58 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.89$ (m, 6H, $CpCH_2CH_2N$); 3.10 (s, 18H, CH_3), 3.54 (m, 6H, $CpCH_2CH_2N$); 4.14 (s, 6H, Cp*H*); 4.18 (s, 15H, Cp*H*); 4.24 (s, 6H, Cp*H*); 4.67 (s, 6H, CH_2Ph); 7.89 (s, 3H, Ph*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 22.2$ ($CpCH_2CH_2N$); 49.0 (CH_3); 64.1 (CH_2Ph); 65.4 ($CpCH_2CH_2N$); 67.5, 68.0, 68.6, 82.8 (Cp–*C*); 129.5, 139.1 (Ph–*C*). Anal. Calc. for $C_{51}H_{66}N_3Br_3Fe_3 \times 2H_2O$ (1164.40 g mol^{-1}): C, 52.96; H, 6.06; N, 3.61 [21]. Found: C, 52.96; H, 6.13; N, 3.62%. $E_{1/2} = 50$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 1.23 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.8. Synthesis of **7** (Fc^4)

The preparation of **7** is similar to that of **5** above (1.00 g (3.89 mmol) 2-(*N*,*N*-dimethylamino)ethylferrocene, 0.20 g (0.44 mmol) 1,2,4,5-tetrakis(bromomethyl)benzene in 25 ml MeCN, stirred for 4 days).

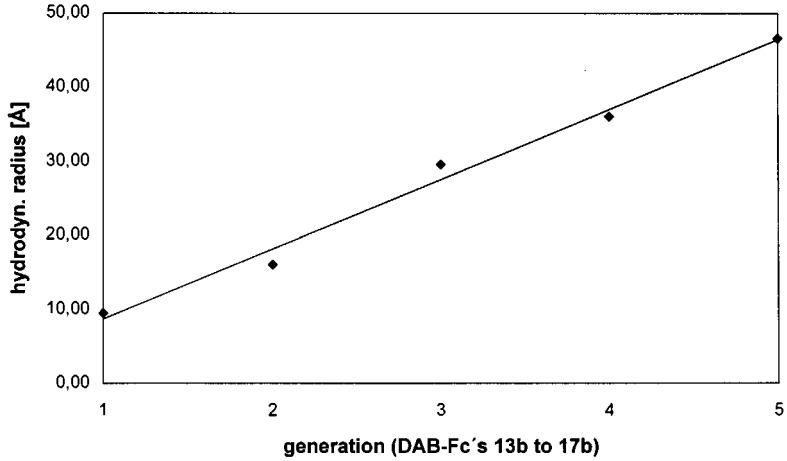


Fig. 2. Plot of hydrodynamic radii versus number of generation of compounds **13b**–**17b**.

Yellow solid. Yield: 84% (0.55 g, 0.37 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.90$ (m, 8H, CpCH_2CH$_2$N); 3.13 (s, 24H, CH_3), 3.97 (m, 8H, CpCH$_2$CH_2N); 4.16 (s, 8H, CpH); 4.24 (s, 20H, CpH); 4.28 (s, 8H, CpH); 5.12 (s, 8H, CH_2Ph); 8.27 (s, 2H, PhH). ^{13}C-NMR (DMSO-d_6): $\delta = 22.2$ (CpCH$_2$CH$_2$N); 48.5 (CH$_3$); 61.7 (CH$_2$Ph); 64.6 (CpCH$_2$$CH_2$N); 67.5, 68.0, 68.6, 82.7 (Cp–C); 131.9, 141.9 (Ph–C). Anal. Calc. for $C_{66}H_{86}N_4Br_4Fe_4 \times 4H_2O$ (1550.52 g mol^{-1}): C, 51.13; H, 6.11; N, 3.61 [21]. Found: C, 51.22; H, 6.18; N, 3.65%. $E_{1/2} = 60$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 1.12 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.9. Synthesis of **11** (1Bz1OH)

A solution of 0.35 g (3.93 mmol) 2-(*N*,*N*-dimethylamino)ethanol in 20 ml MeCN was added slowly to a solution of 1.50 g (5.68 mmol) 1,2-bis(bromomethyl)benzene in 50 ml MeCN at r.t. After the addition the solution turned turbid and the mixture was stirred for 5 h. The precipitate was removed by filtration and the solvent was removed in vacuo. After washing the residue three times with 20 ml Et$_2$O **11** was obtained as white solid. Yield: 30% (0.42 g, 1.19 mmol). ^{1}H-NMR (CD$_3$CN): $\delta = 3.08$ (s, 6H, CH_3); 3.47 (m, 2H, CH_2OH); 4.02 (m, 2H, NCH_2CH$_2$OH); 4.61 (s, 2H, CH_2Ph); 4.66 (s, 2H, CH_2Ph); 4.83 (t, $^3J_{H-H} = 5.5$ Hz, 1H, OH), 7.54 (d, $^3J_{H-H} = 8.2$ Hz, 2H, PhH); 7.60 (d, $^3J_{H-H} = 8.2$ Hz, 2H, PhH). ^{13}C-NMR (CD$_3$CN): $\delta = 33.5$ (BrCH$_2$Ph); 51.4 (CH$_3$); 56.2 (CH$_2$OH); 66.6 (CH$_2$Ph); 68.6 (NCH$_2$CH$_2$OH); 128.8, 130.5, 134.7, 141.7 (Ph–C).

4.10. Synthesis of **8** (Fc^{OH})

The preparation of **8** is similar to that of **5** above (0.20 g (0.78 mmol) 2-(*N*,*N*-dimethylamino)ethylferrocene, 0.20 g (0.57 mmol) **11** in 30 ml MeCN). Yellow solid. Yield: 72% (0.25 g, 0.41 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.85$ (m, 2H, CpCH_2CH$_2$N); 3.04 (s, 6H, CH_3); 3.07 (s, 6H, CH_3); 3.42 (m, 2H, CH_2CH$_2$OH); 3.51 (m, 2H, CpCH$_2$CH_2N); 3.92 (s, 2H, NCH$_2$CH_2OH)); 4.12 (s, 2H, CpH); 4.14 (s, 5H, CpH); 4.18 (s, 2H, CpH); 4.68 (s, 2H, CH_2Ph); 4.70 (s, 2H, CH_2Ph); 5.39 (m, 1H, OH); 7.72 (s, 4H, PhH). ^{13}C-NMR (DMSO-d_6): $\delta = 21.9$ (CpCH$_2$CH$_2$N), 49.2, 49.9 (CH$_3$); 54.9 (CH$_2$OH); 63.6, 65.1, 65.6, 66.6 (NCH$_2$); 67.5, 67.9, 68.6, 82.9 (Cp–C); 130.2, 133.3, 133.5 (PhC). Anal. Calc. for $C_{26}H_{38}N_2Br_2FeO_2$ (610.25 g mol^{-1}): C, 51.17; H, 6.27; N, 4.59. Found: C, 51.03; H, 6.13; N, 4.57%. $E_{1/2} = 40$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 2.38 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.11. Synthesis of **9** (Fc^{2OH})

The preparation of **9** is similar to that of **5** above (0.20 g (0.61 mmol) 1,1′-bis(2-(*N*,*N*-dimethylamino)-ethyl)ferrocene, 0.78 g (2.20 mmol) **11** in 70 ml MeCN). Yellow solid. Yield: 79% (0.52 g, 0.48 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.91$ (m, 4H, CpCH_2CH$_2$N); 3.07 (s, 12H, CH_3); 3.12 (s, 12H, CH_3); 3.45 (m, 4H, CH_2CH$_2$OH); 3.63 (m, 4H, CpCH$_2$CH_2N); 3.92 (s, 4H, NCH$_2$CH_2OH); 4.16 (s, 4H, CpH); 4.27 (s, 4H, CpH); 4.71 (s, 2H, CH_2Ph); 4.81 (s, 2H, CH_2Ph); 5.39 (s br, 2H, OH); 7.74 (s br, 8H, PhH). ^{13}C-NMR (DMSO-d_6): $\delta = 22.0$ (CpCH$_2$CH$_2$N), 49.1, 49.9 (CH$_3$); 54.9 (CH$_2$OH); 63.7, 65.0, 65.2, 66.5 (NCH2); 68.3, 68.8, 83.3 (Cp–C); 130.1, 133.3, 133.5 (PhC). Anal. Calc. for $C_{42}H_{66}N_4Br_4FeO_2 \times 0.5H_2O$ (1043.50 g mol^{-1}): C, 48.34; H, 6.47; N, 5.37 [21]. Found: C, 48.30; H, 7.09; N, 5.34%. $E_{1/2} = 80$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 1.31 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.12. Synthesis of **12** (1Bz2OH)

The preparation of **12** is similar to that of **11** above (0.30 g (3.36 mmol) 2-(*N*,*N*-dimethylamino)ethanol in 20 ml MeCN, 1.50 g (4.20 mmol) 1,3,5-tris(bromomethyl)benzene in 50 ml MeCN). White solid. Yield: 21% (0.31 g, 0.70 mmol). ^{1}H-NMR (DMSO-d_6): $\delta =$ 3.04 (s, 6H, CH_3); 3.41 (s, 2H, NCH_2CH$_2$OH); 3.91 (s, 2H, NCH$_2$CH_2OH); 4.67 (s, 2H, PhCH_2N); 4.74 (s, 4H, PhCH_2Br); 5.40 (s br, 1H, OH); 7.62 (s, 1H, PhH); 7.68 (s, 2H, PhH). ^{13}C-NMR (DMSO-d_6): $\delta = 33.2$ (PhCH$_2$Br); 49.9 (CH$_3$); 54.9 (NCH$_2$$CH_2$OH); 65.1, 66.8 (N$CH_2$); 129.1, 131.6, 133.8, 139.3 (PhC).

4.13. Synthesis of **10** ($2Fc^{OH}$)

The preparation of **10** is similar to that of **5** above (0.30 g (1.17 mmol) 2-(*N*,*N*-dimethylamino)ethylferrocene, 0.25 g (0.56 mmol) **12** in 50 ml MeCN). Yellow solid. Yield: 84% (0.45 g, 0.47 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.89$ (s, 4H, CpCH_2CH$_2$N); 3.13 (s, 6H, CH_3); 3.16 (s, 12H, CH_3); 3.50 (s, 2H, NCH_2CH$_2$OH); 3.57 (s, 4H, CpCH$_2$CH_2N); 3.91 (s, 2H, CH_2OH); 4.12 (s, 4H, CpH); 4.20 (s, 10H, CpH); 4.26 (s, 4H, CpH); 4.74 (s br, 6H, PhCH_2); 5.40 (s, 1H, OH); 7.96 (s, 3H, PhH). ^{13}C-NMR (DMSO-d_6): $\delta =$ 22.3 (CpCH$_2$CH$_2$N); 49.1, 50.0 (CH$_3$); 54.9 (CH$_2$OH); 63.8, 64.8, 65.3, 66.1 (NCH$_2$); 68.1, 68.6, 69.2, 82.8 (Cp–C); 129.5, 139.1, 139.2 (Ph–C). Anal. Calc. for $C_{41}H_{58}N_3Br_3Fe_2O \times 2H_2O$ (996.38 g mol^{-1}): C, 49.42; H, 6.27; N, 4.22 [21]. Found: C, 49.76; H, 6.46; N, 4.45%. $E_{1/2} = 40$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 1.54 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.14. Synthesis of **13a** (DAB–Fc-4)

A solution of 0.48 g (1.52 mmol) DAB–Am-4 and 1.30 g (6.07 mmol) formyl ferrocene in 50 ml toluene was heated to reflux for 6 h. After removing the solvent in vacuo the residue was solved in 50 ml EtOH. $NaBH_4$ (0.5 g) was added to the mixture which was heated to reflux for 4 h. The solvent was removed in vacuo and the residue was suspended in 70 ml CH_2Cl_2. The organic layer was washed three times with 50 ml water and dried over Na_2SO_4. After removing the solvent **13a** was obtained as a red wax-like solid. Yield: 92% (1.55 g, 1.40 mmol). ^{1}H-NMR ($CDCl_3$): $\delta = 1.33$ (m, 4H, $NCH_2CH_2CH_2CH_2N$); 1.59 (m, 8H, $NCH_2CH_2CH_2$-NH); 2.34 (m, 4H, $NCH_2CH_2CH_2CH_2N$); 2.40 (m, 8H, $NCH_2CH_2CH_2NH$); 2.59 (t, $^3J_{H-H} = 7.1$ Hz, 8H, $NCH_2CH_2CH_2NH$); 3.48 (s, 8 H, $CpCH_2$), 4.07 (s, 8H, Cp*H*); 4.09 (s, 20H, Cp*H*); 4.16 (s, 8H, Cp*H*). ^{13}C-NMR ($CDCl_3$):$\delta = 24.9$ ($NCH_2CH_2CH_2CH_2N$); 27.5 ($NCH_2CH_2CH_2NH$); 48.3, 49.2 (CH_2NHCH_2); 52.3 ($NCH_2CH_2CH_2NH$); 54.0 ($NCH_2CH_2CH_2CH_2N$); 67.9, 68.4, 68.5, 86.7 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 1109$ [M^+]. $E_{1/2} = 30$ mV ($CH_2Cl_2 + 0.1$ M TBAPF; vs. fc/fc^+).

4.15. Synthesis of **13b** (DAB–Fc-4 × 6HCl)

Through a stirred solution of 0.40 g (0.36 mmol) DAB–Fc-4 in 50 ml CH_2Cl_2/Et_2O (4:1) a gentle stream of HCl gas was bubbled for 60 min. During this time a yellow precipitate was formed. Afterwards the mixture was stirred another 30 min. The solvent was removed in vacuo and the residue was washed twice with 20 ml Et_2O. Compound **13b** was obtained as a yellow solid. Yield: 81% (0.38 g, 0.29 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 1.78$ (s, 4H, $NHCH_2CH_2CH_2CH_2NH$); 2.13 (s, 8H, $NHCH_2CH_2CH_2NH_2$); 2.89 (s, 8H, $NHCH_2CH_2$-CH_2NH_2); 3.06 (m, 4H, $NHCH_2CH_2CH_2CH_2NH$); 3.17 (s, 8H, $NHCH_2CH_2CH_2NH_2$); 3.92 (s, 8H, $CpCH_2$), 4.21 (s, 20H, Cp*H*); 4.22 (s, 8H, Cp*H*); 4.46 (s, 8H, Cp*H*); 9.38 (s, 8H, NH_2); 11.13 (s, 2H, N*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 19.6$ ($NHCH_2CH_2CH_2NH_2$); 19.9 ($NHCH_2CH_2CH_2CH_2NH$); 42.9, 46.0 ($CH_2NH_2CH_2$); 49.0 ($NHCH_2CH_2CH_2NH_2$); 50.6 ($NHCH_2CH_2$-CH_2CH_2NH); 68.7, 70.7, 76.5 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 1109$ [$M^+ - 6$HCl]. Anal. Calc. for $C_{60}H_{86}N_6Cl_6Fe_4 \times 4H_2O$ (1399.60 g mol^{-1}): C, 51.49; H, 6.77; N, 6.00 [21]. Found: C, 51.36; H, 6.86; N, 5.83%. $E_{1/2} = 90$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc^+). $D = 1.17 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.16. Synthesis of **14a** (DAB–Fc-8)

The preparation of **14a** is similar to that of **13a** above (0.54 g (0.70 mmol) DAB–Am-8 and 1.19 g (5.56 mmol) formyl ferrocene, 0.55 g (14.5 mmol) $NaBH_4$). Red wax-like solid. Yield: 89% (1.47 g, 0.62 mmol). ^{1}H-NMR ($CDCl_3$): $\delta = 1.34$ (s, 4H, $NCH_2CH_2CH_2$-CH_2N); 1.51 (m, 8H, $NCH_2CH_2CH_2N$); 1.59 (m, 16H, $NCH_2CH_2CH_2NH$); 2.35 (m, 20H, $NCH_2CH_2CH_2N$ and $NCH_2CH_2CH_2CH_2N$); 2.41 (m, 16H, NCH_2-CH_2CH_2NH); 2.59 (t, $^3J_{H-H} = 7.1$ Hz, 16H, $NCH_2CH_2CH_2NH$); 3.47 (s, 16H, $CpCH_2$), 4.07 (s, 16H, Cp*H*); 4.09 (s, 40H, Cp*H*); 4.15 (s, 16H, Cp*H*). ^{13}C-NMR ($CDCl_3$): $\delta = 24.4$ ($NCH_2CH_2CH_2N$); 25.1 ($NCH_2CH_2CH_2CH_2N$); 27.5 ($CH_2CH_2CH_2NH$); 48.2, 49.2 (CH_2NHCH_2); 52.2 ($NCH_2CH_2CH_2NH$); 52.4 ($NCH_2CH_2CH_2N$); 54.3 ($NCH_2CH_2CH_2CH_2N$); 67.7, 68.4, 68.8, 86.9 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 2360$ [M^+]. $E_{1/2} = 30$ mV ($CH_2Cl_2 + 0.1$ M TBAPF; vs. fc/fc^+).

4.17. Synthesis of **14b** (DAB–Fc-8 × 14HCl)

The preparation of **14b** is similar to that of **13b** above (0.54 g (0.23 mmol) DAB–Fc-8 in 50 ml CH_2Cl_2/Et_2O (1:1)). Yellow solid. Yield 83% (0.54 g, 0.19 mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 1.85$ (s, 4H, $NHCH_2$-$CH_2CH_2CH_2NH$); 2.16 (s, 16H, $NHCH_2CH_2CH_2NH_2$); 2.24 (s; 8H, $NHCH_2CH_2CH_2NH$); 2.93 (s, 16H, $NHCH_2CH_2CH_2NH_2$); 3.26 (s, 36H, CH_2NHCH_2); 3.95 (s, 16H, $CpCH_2$), 4.22 (s, 40H, Cp*H*); 4.24 (s, 16H, Cp*H*); 4.48 (s, 16H, Cp*H*); 9.40 (s, 16H, NH_2); 11.16 (s, 6H, N*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 15.1$, 17.1, 19.7 ($CH_2CH_2CH_2CH_2$ and $CH_2CH_2CH_2$); 42.9, 46.0 ($CH_2NH_2CH_2$); 48.4, 49.2, 52.0, ($NHCH_2$); 68.7, 70.7, 76.5 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 2360$ [$M^+ - 14$HCl]. Anal. Calc. for $C_{128}H_{190}N_{14}Cl_{14}Fe_8 \times 4H_2O$ (2940.31 g mol^{-1}): C, 52.29; H, 6.79; N, 6.67 [21]. Found: C, 52.11; H, 6.83; N, 6.67%. $E_{1/2} = 90$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc^+). $D = 0.69 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.18. Synthesis of **15a** (DAB–Fc-16)

The preparation of **15a** is similar to that of **13a** above (0.38 g (0.23 mmol) DAB–Am-16 and 0.77 g (3.60 mmol) formyl ferrocene, 0.3 g (7.9 mmol) $NaBH_4$). Red wax-like solid. Yield: 78% (0.89 g, 0.18 mmol). ^{1}H-NMR ($CDCl_3$): $\delta = 1.54$ (s br, 28H, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 1.62 (m, 32H, $NCH_2CH_2CH_2NH$); 2.37 (m, 52H, NCH_2); 2.44 (m, 32H, $NCH_2CH_2CH_2$-NH); 2.62 (t, 32H, $^3J_{H-H} = 6.9$ Hz, $NCH_2CH_2CH_2NH$); 3.49 (s, 32H, $CpCH_2$); 4.10 (s, 32H, Cp*H*); 4.12 (s, 80H, Cp*H*); 4.18 (s, 32H, Cp*H*).^{13}C-NMR ($CDCl_3$): $\delta =$ 24.3, 24.6, 27.5 ($CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 48.3, 49.2, 52.2; 52.4, 53.4 (CH_2NCH_2 and CH_2-$NHCH_2$); 67.7, 68.4, 68.5, 87.0 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 4851$ [M^+]. $E_{1/2} = 50$ mV ($CH_2Cl_2 + 0.1$ M TBAPF; vs. fc/fc^+).

4.19. Synthesis of **15b** (DAB–Fc-16 × 30HCl)

The preparation of **15b** is similar to that of **13b** above (0.30 g (6.2×10^{-2} mmol) DAB–Fc-16 in 50 ml CH_2Cl_2/Et_2O (1:2)). Yellow solid. Yield: 81% (0.30 g, 5.0×10^{-2} mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.20$ (s br, 64H, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 2.96 (s, 32H, $NHCH_2CH_2CH_2NH_2$); 3.36 (s br, 84H, CH_2NHCH_2); 4.07 (s, 32H, $CpCH_2$), 4.12 (s, 80H, Cp*H*); 4.23 (s, 32H, Cp*H*); 4.50 (s, 32H, Cp*H*); 9.45 (s, 32H, NH_2); 11.14 (s, 14H, N*H*). ^{13}C-NMR (DMSO-d_6): $\delta = 17.0$, 19.6 ($CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 42.9, 46.1, 49.2 ($CH_2NH_2CH_2$ and CH_2NHCH_2); 68.1, 70.8, 76.5 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z =$ 4851 [M^+–30HCl]. $E_{1/2} = 90$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 0.37 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.20. Synthesis of **16a** (DAB–Fc-32)

The preparation of **16a** is similar to that of **13a** above (0.55 g (0.16 mmol) DAB–Am-32 and 1.08 g (5.05 mmol) formyl ferrocene, 0.55 g (14.5 mmol) $NaBH_4$). Red wax-like solid. Yield: 88% (1.42 g, 0.14 mmol). ^{1}H-NMR ($CDCl_3$): $\delta = 1.53$ (s br, 60H, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 1.59 (m, 64H, $CH_2CH_2CH_2NH$); 2.35 (s br, 116H, NCH_2); 2.41 (m, 64H, $CH_2CH_2CH_2NH$); 2.60 (m, 64H, $CH_2CH_2CH_2NH$); 3.47 (s, 64H, $CpCH_2$); 4.08 (s, 64H, Cp*H*); 4.10 (s, 160H, Cp*H*); 4.16 (s, 64H, Cp*H*). ^{13}C-NMR ($CDCl_3$): $\delta = 24.3$, 27.4 ($CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 48.2, 49.1, 52.4 (CH_2NHCH_2 and $CH_2NH_2CH_2$); 67.8, 68.4, 68.5, 86.8 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 9540$ broad [M^+], Calc. 9851 (for $C_{536}H_{752}N_{62}Fe_{32}$). $E_{1/2} = 20$ mV (CH_2Cl_2 + 0.1 M TBAPF; vs. fc/fc$^+$).

4.21. Synthesis of **16b** (DAB–Fc-32 × 62HCl)

The preparation of **16b** is similar to that of **13b** above (0.80 g (8.1×10^{-2} mmol) DAB × Fc-32 in 50 ml CH_2Cl_2/Et_2O (3:4)). Yellow solid. Yield: 83% (0.81 g, 6.7×10^{-2} mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.29$ (s br, 64H, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 2.96 (s, 64H, $NHCH_2CH_2CH_2NH_2$); 3.40 (s br, 188H, CH_2NHCH_2); 4.03 (s, 64H, $CpCH_2$); 4.26 (s, 224H, Cp*H*); 4.57 (s, 64H, Cp*H*); 9.45 (s, 64H, NH_2); 11.14 (s, 30H, N*H*). [22] ^{13}C-NMR (DMSO-d_6): $\delta = 19.7$ (br, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 43.1, 46.1, 49.2 (br, CH_2NHCH_2 and $CH_2NH_2CH_2$) 68.8, 70.9, 76.5 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 9460$ broad [M^+], Calc. 9851 (for $C_{536}H_{752}N_{62}Fe_{32}$ without 62HCl). $E_{1/2} = 90$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 0.31 \times 10^{-6}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

4.22. Synthesis of **17a** (DAB–Fc-64)

The preparation of **17a** is similar to that of **13a** above (0.50 g (7.0×10^{-2} mmol) DAB–Am-64 and 0.96 g (4.48 mmol) formyl ferrocene, 0.55 g (14.5 mmol) $NaBH_4$). Red wax-like solid. Yield: 93% (1.29 g, 6.5×10^{-2} mmol). ^{1}H-NMR ($CDCl_3$): $\delta = 1.52$ (s br, 124H, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 1.58 (m, 128H, $CH_2CH_2CH_2NH$); 2.36 (s br, 244H, NCH_2); 2.41 (m, 128H, $CH_2CH_2CH_2NH$); 2.60 (m, 128H, $CH_2CH_2CH_2NH$); 3.47 (s, 128H, $CpCH_2$); 4.08 (s, 128H, Cp*H*); 4.10 (s, 320H, Cp*H*); 4.16 (s, 128H, Cp*H*). ^{13}C-NMR ($CDCl_3$): $\delta = 24.3$, 27.5 ($CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 48.2, 49.2, 52.2 (CH_2NHCH_2 and CH_2NCH_2); 67.8, 68.4, 68.5, 86.9 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 18400$ broad [M^+], Calc. 19842 (for $C_{1080}H_{1520}N_{126}Fe_{64}$). $E_{1/2} = 10$ mV (CH_2Cl_2 + 0.1 M TBAPF; vs. fc/fc$^+$).

4.23. Synthesis of **17b** (DAB–Fc-64 × 126HCl)

The preparation of **17b** is similar to that of **13b** above (1.02 g (5.1×10^{-2} mmol) DAB–Fc-64 in 80 ml CH_2Cl_2/Et_2O (1:1)). Yellow solid. Yield: 82% (1.02 g, 4.2×10^{-2} mmol). ^{1}H-NMR (DMSO-d_6): $\delta = 2.31$ (s br, 252H, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 3.08 (s br, 128H, $NHCH_2CH_2CH_2NH_2$); 3.41 (s br, 372H, CH_2NHCH_2); 4.06 (s, 128H, $CpCH_2$); 4.28 (s, 448H, Cp*H*); 4.59 (s, 128H, Cp*H*); 9.48 (s br, 128H, NH_2); 11.14 (s br, 60H, N*H*). [22] ^{13}C-NMR (DMSO-d_6): $\delta = 15.1$, 19.7 (br, $CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2$); 43.1, 46.1, 49.0 (br $CH_2NH_2CH_2$ and CH_2NHCH_2) 68.8, 70.8, 76.5 (Cp–*C*). MS (MALDI-TOF, DHB): $m/z = 18150$ broad [M^+], Calc. 19842 (for $C_{1080}H_{1520}N_{126}Fe_{64}$ without 126HCl). Anal. Calc. for $C_{1080}H_{1646}N_{126}Cl_{126}Fe_{64}$ (24436.19 g mol^{-1}): C, 53.08; H, 6.79; N, 7.22. Found: C, 52.99; H, 7.07; N, 7.28%. $E_{1/2} = 90$ mV (DMSO + 0.1 M TBAPF; vs. fc/fc$^+$). $D = 0.24 \times 10^{-7}$ cm^2 s^{-1} (DMSO + 0.1 M TBAPF).

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