Tris(1,10-phenanthroline)iron(II) Complexes – Broad Variation of the Redox Potential by 4,7-Substitution at the Phenanthroline Ligands[1]

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The new 4,7-donor-substituted phenanthrolines **2a–h** were synthesized and the corresponding tris(1,10-phenanthroline)iron(II) complexes **3a–h** studied by cyclic voltammetry. In more detail three novel aza-crown ether-linked (phenanthroline)iron complexes were investigated, the redox potentials of which could be fine-tuned by the addition of group-Ia,IIa metal cations. All iron(II) complexes showed reversible waves at scan rates between 50 and 500 mV · s^{-1} and could be reversibly oxidized and reduced by chemical means.

Our continued interest[2] in developing new reactions by applying electron-transfer concepts has emphasized the necessity to prepare a series of structurally related, stable one-electron transfer reagents that exhibit a broad variation in their redox potentials. At first glance, triarylamines and their cation radicals seem to fulfill the desired criteria. By variation of the substitution pattern in the aromatic rings, a whole series of redox systems was synthesized by Steckhan[3] that cover the wide potential range from 0.12 to 1.33 V vs. ferrocene/ferrocenium[4]. However, the triarylamine cation radical redox systems display three decisive disadvantages as mechanistic probes for electron transfer: (1) not all of the cation radical salts prove to be sufficiently stable[3b], (2) they show Lewis acid activity[3b], and (3) in some cases they promote inner-sphere electron transfer via intermediate complexes[3b,5]. To circumvent these problems we have turned our attention to the synthesis of tris(1,10-phenanthroline)Fe^{II}/Fe^{III} redox systems. According to studies by Kochi[6] they behave as clean outer-sphere electron transfer reagents and since the metal ions are well shielded by the chelating 1,10-phenanthroline rings no significant Lewis acid activity is expected.

Surprisingly, despite the fact that (phenanthroline)metal complexes have been playing an substantial role in analytical chemistry[7], in solar energy conversion[8,9], and more recently in Heck reactions[10], relatively little effort has been invested to control the electronic situation of the complex by variation of the substituents in the 4,7-positions. An obvious reason for this omission is the difficulty to synthesize the corresponding substituted 1,10-phenanthrolines by a simple strategy. As a consequence, only a narrow range of potentials (0.4–0.9 V vs. ferrocene/ferrocenium) has been covered by (trisphenanthroline)iron complexes until recently when the potentials of two tris(4,7-diamino-substituted phenanthroline)iron complexes were reported by us[11]. Since it became obvious from our work, that the redox potentials of tris(phenanthroline)iron complexes could decisively be modulated by substitution in the 4,7-positions of the phenanthroline ligands, we decided to explore the influence of other donor substituents on the redox behavior.

Results and Discussion

As described earlier[11], the best approach to a variety of 4,7-donor-substituted phenanthrolines is by nucleophilic aromatic substitution of chlorine in 4,7-dichlorophenanthroline (**1**), which can be obtained from 1,2-diaminobenzene in a high-yield (50% overall) five-step synthesis. The nucleophilic substitution itself can readily be accomplished with the amine or sulfide component in excess at elevated temperatures (Scheme 1). Table 1 lists all 4,7-disubstituted 1,10-phenanthrolines **2a–h** synthesized in this work and the ^{1}H-NMR signals of the 1,10-phenanthroline moiety. The ^{1}H-NMR and all other analytical data clearly support the assignment of 4,7-disubstituted phenanthrolines.

From the new 1,10-phenanthrolines listed in Table 1, we have synthesized the corresponding iron(II) complexes using a modification of a literature procedure[11]. Thus, a solution of the 1,10-phenanthrolines **2a–h** in an organic solvent/water mixture was treated with $FeSO_4 \cdot 7\ H_2O$, and from the intensely red-colored solutions the red salts were precipitated by addition of ammonium, potassium, or caesium hexafluorophosphate. The complexes were identified by their characteristic strong UV absorption maxima between 522 and 544 nm, their ^{1}H- and ^{13}C-NMR spectra.

All iron(II)/iron(III) redox couples exhibited clean and reversible waves (between 50 and 500 mV · s^{-1}) in the cyclic voltammetry experiment and fulfilled other criteria for complete reversibility: (1) $E^{ox}_{1/2}$ is independent of the scan rate; (2) the peak current ratio i_c/i_a is 1.00 ± 0.05; (3) the separation of the cathodic and anodic peaks is 60 ± 5 mV except for **3b**, **3c** and **3f**; (4) $i_{pa} \cdot v^{-1/2}$ is constant (Table 3). In addition, the iron(II) complexes could be chemically

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Scheme 1

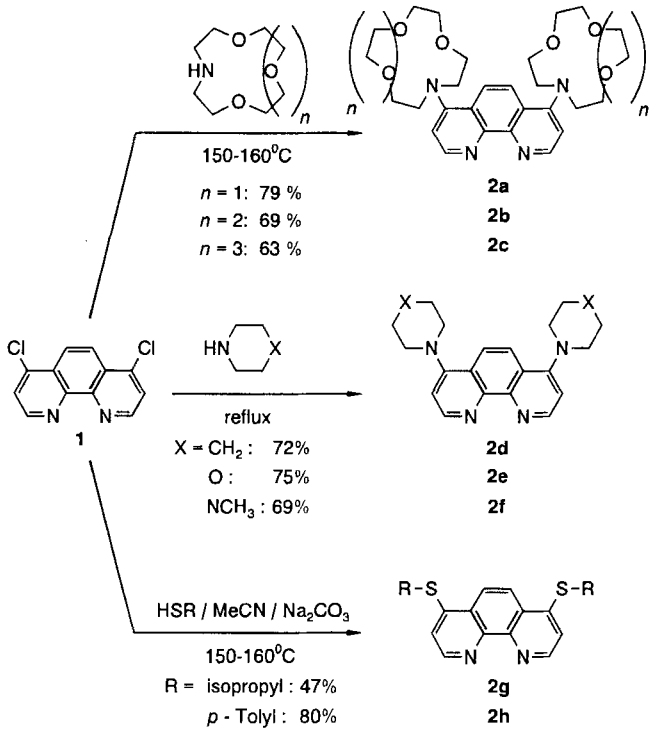
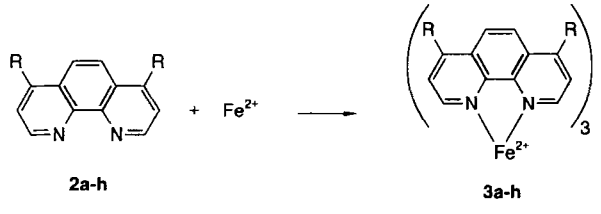


Table 1. Yields of the 4,7-disubstituted 1,10-phenanthrolines **2a–h** and ^{1}H-NMR shifts of the phenanthroline moiety

2	Yield (%)	^{1}H NMR ($CDCl_3$)		
		d, 2 H (*J* in Hz) 3-H, 8-H	s, 2 H 5-H, 6-H	d, 2 H (*J* in Hz) 2-H, 9-H
2a	79	7.08 (5.2)	8.37	8.89 (5.2)
2b	69	7.25 (5.2)	8.04	8.91 (5.2)
2c	63	7.28 (5.2)	8.07	8.93 (5.2)
2d	72	7.06 (6.0)	7.93	8.93 (6.0)
2e	75	7.11 (6.0)	7.99	9.02 (6.0)
2f	69	7.10 (6.0)	7.97	8.99 (6.0)
2g	47	7.47 (4.9)	8.18	8.97 (4.9)
2h	80	6.95 (4.9)	8.26	8.81 (4.9)



oxidized to the iron(III) complexes with chlorine and reduced again to iron(II) by using hydroxylamine or hydrazine. Together with known (phenanthroline)iron(II) complexes[7] the wide potential range of $E^{ox}_{1/2}$ (vs. Fc/Fc^+) = −0.23 (**3m**) to 1.25 V [tris(5-nitrophenanthroline)iron(II) hexafluorophosphate] is now readily accessible.

While the tris(phenanthroline)iron complexes **3d–m** may serve as standard one-electron redox systems with fixed potential, the aza-crown ether-substituted variants **3a–c** should allow fine-tuning of the redox potential within certain limits upon addition of group Ia, IIa metal cations. In comparison with the aza-crown ether-linked ferrocenes described by Beer[12], we anticipated to capture an enlarged response to the electrochemical potential in our iron complexes because six coordination sites linked to one single redox center are available. Upon addition of various alkali metal ions, however, the shift of the redox potential proved to be much smaller than expected, at most 140–150 mV (Figure 1).

Characteristically, for **3a–c** a large amount of M^+ is needed to effect a sizable shift in $E^{ox}_{1/2}$. For example, the maximum $\Delta E^{ox}_{1/2}$ is reached with **3c** upon addition of about 10 equivalents[13,14] of K^+, in the case of **3b** with about 60 equivalents of Na^+, but with **3a** not even with 250 equiva-

Table 2. ^{1}H-NMR data of the tris(phenanthroline)iron complexes **3a–h**

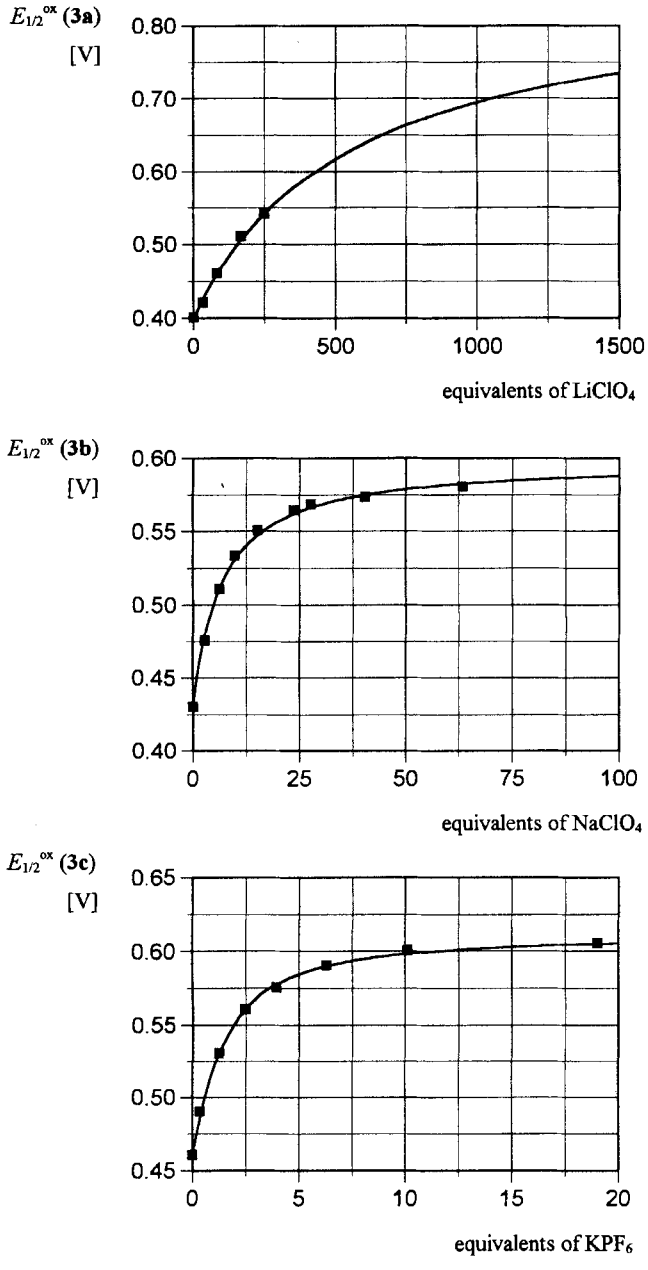
3	^{1}H NMR ($CDCl_3$)		
	d, 6 H (*J* in Hz) 3-H, 8-H	s, 6 H 5-H, 6-H	d, 6 H (*J* in Hz) 2-H, 9-H
3a	6.97 (6.0)	8.65	7.30 (6.0)
3b	7.04 (6.1)	8.35	7.27 (6.1)
3c	7.21 (6.0)	8.20	7.39 (6.0)
3d	7.03 (7.0)	7.90	7.40 (7.0)
3e	6.85 (6.0)	7.87	7.21 (6.0)
3f	6.97 (7.0)	7.93	7.31 (7.0)
3g	6.90 (5.6)	8.26	7.25 (5.6)
3h	7.47 (5.6)	8.19	7.57 (5.6)

Table 3. Cyclic voltammetry data and redox potentials[a] of tris(1,10-phenanthroline)iron(II) hexafluorophosphates **3a–h** in acetonitrile

3	Substituent in 4, 7 - positions	$E_{1/2}{}^{ox}$ [a] [V]	i_a/i_c [b]	ΔE_p [c] [mV]
3a	aza[12]crown-4	0.01	0.99	60
3b	aza[15]crown-5	0.04	0.97	70
3c	aza[18]crown-6	0.08	0.98	80
3d	piperidine	0.13	1.00	60
3e	morpholine	0.22	1.00	60
3f	*N*-methylpiperazine	0.23	1.00	70
3g	isopropylthio	0.56	1.00	65
3h	*p*-methylphenylthio	0.61	1.00	65
3i[d]	H	0.69	1.00	57
3j[d]	O-*p*-C_6H_5	0.47	1.00	60
3k[d]	OMe	0.38	1.00	55
3l[d]	NEt_2	-0.09	1.00	60
3m[d]	$NH(CH_2)_3NH_2$	-0.23	1.00	60

[a] All potentials are referenced to ferrocene/ferrocenium, v = 100 mV · s^{-1}. – [b] Ratio of the anodic to cathodic peak current of **3**. – [c] Peak-to-peak separation of **3**. – [d] Examples from ref.[11].

Figure 1. Dependence of $E_{1/2}^{ox}$ in **3a–c** as a function of added alkali metal ions[13]; the data points can be nicely fitted to the theoretical equation[14] describing the effect of metal ion complexation on the redox potential shift



lents of Li^+. Hence, the smaller the aza-crown ether subunit, the less it is prone to complex the metal ion, that usually is well bound in an unimpeded environment, e.g. aza[12]-crown-4/Li^+, aza[15]crown-5/Na^+, aza[18]crown-6/K^+[15]. Most likely, the reduced complexation ability is caused by the interference of the 5- and 6-protons at the phenanthroline system with the 4,7-crown ether units, thus preventing the cyclic subunits from adopting the optimum conformation for complexation of group-Ia metal ions[16]. Obviously, the restrain in conformational freedom is more pronounced the smaller the aza-crown ether. Addition of NH_4^+ to **3c** proved to be a little bit more effective, since we registered a $\Delta E_{1/2}^{ox}$ of 170 mV in the presence of 15 equivalents, which is 30 mV more than with K^+. Apparently, NH_4^+ can bind stronger to the nitrogen atom of the aza-crown ether by means of hydrogen bonds than K^+. Only a very weak effect on $E_{1/2}^{ox}$ (<30 mV) was observed with **3c**/Na^+ or **3c**/Cs^+, indicating once again the restrained flexibility of the crown ether subunits. Nevertheless, while the poor binding of M^+ to **3a–c** is certainly prohibitive to their use in sensor systems, they constitute readily tunable redox reagents, that do not depend too critically on the amount of added cations.

In line with the results above no significant potential shifts were observed upon addition of $Mg(ClO_4)_2$ to **3a** or **3b**. Hence, it was very much a surprise to learn, that **3c** exhibited a drastic shift in $E_{1/2}^{ox}$ of 370 mV upon addition of only one equivalent of Ba^{2+}[17], a remarkable shift when compared with $\Delta E_{1/2}^{ox} = 60$ mV upon addition of one equivalent of K^+. This result suggests, because of the almost identical ion radii of K^+ and Ba^{2+}, that with **3c** differentiation by ion size is only a minor factor governing the binding constant and that Coulomb attraction (the charge to radius values for K^+ and Ba^{2+} are $0.72 \cdot 10^{-2}$ and $1.48 \cdot 10^{-2}$ As · pm^{-1}, respectively) may become the decisive driving force for inducing the right conformation in aza-crown ether units, when their conformational freedom in the uncomplexed state is restricted. Interestingly, this may be a viable strategy for the design of highly selective sensor systems.

In conclusion, a new series of stable one-electron transfer reagents based on 4,7-disubstituted (phenanthroline)-iron(II) complexes is presented the potentials of which can now be varied in small steps over a wide potential range ($E_{1/2}^{ox} = -0.23$ to $+1.25$ V vs. Fc/Fc^+). In addition, compounds **3a–c** may be used as tunable redox systems in homogeneous electron-transfer reactions.

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Experimental

General remarks: See ref.[11]. The cyclic voltammograms of all Fe^{II}/Fe^{III} couples were measured by using the standard three-electrode set-up (Pt working and Pt auxiliary electrode, silver wire as reference electrode) connected to a Princeton Applied Research Model 362 potentiostat. The experiments were carried out on a 1 mM solution of the iron salt in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials were measured at a scan rate of 100 mV · s^{-1} and are referenced to internal 2,4,6-triphenylpyrylium tetrafluoroborate, that has $E_{1/2} = -0.68$ V vs. ferrocene/ferrocenium. – 4,7-Dichloro-1,10-phenanthroline (**1**) was prepared according to a modified procedure[11] originally described by Snyder and Freier[18].

4,7-Bis(4,7,10-trioxa-1-azacyclododecyl)-1,10-phenanthroline (**2a**): A mixture of 4,7-dichloro-1,10-phenanthroline (**1**) (145 mg, 0.580 mmol) and aza[12]crown-4 (470 mg, 2.680 mmol) was stirred at 160°C for 1 h. The reaction mixture was cooled to room temp., dissolved in 5 ml of dichloromethane and the solution washed with 5 ml of a K_2CO_3 solution (20%). The organic layer was dried with $MgSO_4$, and the solvent was distilled off. The residue was dissolved

in 1.5 ml of dichloromethane, and the product was precipitated from the solution by addition of hexane as a light brown, highly viscous oil, which was washed several times with hexane and dried in vacuo to yield 243 mg (79%) of **2a**. – IR (KBr): $\tilde{\nu}$ = 3421 cm^{-1} (OH), 3088 (CH aromat.), 2911, 2856 (CH aliphat.), 1560, 1516 (CC aromat.), 1131 (CO). – ^1H NMR ($CDCl_3$): δ = 3.63 (t, *J* = 4.6 Hz, 8H, 2′,2″,12′,12″-H), 3.73 (s, 16H, 5′,5″,6′,6″,8′,8″,9′,9″-H), 3.86 (t, *J* = 4.6 Hz, 8H, 3′,3″,11′,11″-H), 7.08 (d, *J* = 5.2 Hz, 2H, 3,8-H), 8.37 (s, 2H, 5,6-H), 8.89 (d, *J* = 5.2 Hz, 2H, 2,9-H). – ^{13}C-NMR ($CDCl_3$): δ = 53.5 (t, C-2′,2″,12′,12″), 69.6 (t, C-3′,3″,11′,11″), 71.1 (t, C-5′,5″,9′,9″), 71.3 (t, C-6′,6″,8′,8″), 111.5 (d, C-3,8), 121.3 (d, C-5,6), 123.6 (s, C-4a,6a), 148.7 (s, C-1a,10a), 149.6 (d, C-2,9), 155.8 (s, C-4,7).

4,7-Bis(4,7,10,13-tetraoxa-1-azacyclopentadecyl)-1,10-phenanthroline (**2b**): A mixture of **1** (156 mg, 0.630 mmol) and aza[15]-crown-5 (550 mg, 2.50 mmol) was stirred at 150–160°C for 2 h. The reaction mixture was cooled to room temp., dissolved in 5 ml of dichloromethane and the solution washed with 5 ml of a K_2CO_3 solution (20%). The organic layer was dried with $MgSO_4$, and the solvent was removed. Then excess aza[15]crown-5 was distilled off in vacuo. The residue was purified by column chromatography [silica gel (20 x 2 cm); MeOH/2 N NH_4Cl solution/MeCN, 7:2:1], and the eluate was extracted twice with chloroform. The combined organic layers were washed with 5 ml of a K_2CO_3 solution (20%) and dried with $MgSO_4$. The solvent was evaporated and the light brown viscous oil dried in vacuo to yield 268 mg (69%) of **2b**. – IR (KBr): $\tilde{\nu}$ = 3422 cm^{-1} (OH), 3088 (CH aromat.), 2864 (CH aliphat.), 1560, 1517 (CC aromat.), 1116 (CO). – ^1H NMR ($CDCl_3$): δ = 3.69–3.78 (m, 40H, CH_2) 7.25 (d, *J* = 5.2 Hz, 2H, 3,8-H), 8.04 (s, 2H, 5,6-H), 8.91 (d, *J* = 5.2 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 53.5 (t, C-2′,2″,15′,15″), 69.5 (t, C-3′,3″,14′,14″), 70.6 (t, C-5′,5″,6′,6″,11′,11″,12′,12″), 71.0 (t, C-8′,8″,9′,9″), 112.6 (d, C-3,8), 121.0 (d, C-5,6), 123.4 (s, C-4a,6a), 148.5 (s, C-1a,10a), 149.8 (d, C-2,9), 156.0 (s, C-4,7).

4,7-Bis(4,7,10,13,16-pentaoxa-1-azacyclooctadecyl)-1,10-phenanthroline (**2c**): A mixture of **1** (150 mg, 0.600 mmol) and aza[18]-crown-6 (630 mg, 2.40 mmol) was stirred at 150–160°C for 1.5 h. The reaction mixture was cooled to room temp., dissolved in 5.0 ml of dichloromethane and the solution washed with 5 ml of a Na_2CO_3 solution (20%). The organic layer was dried with $MgSO_4$, and the solvent was removed. Then excess aza[18]crown-6 was distilled off in vacuo. The residue was purified by chromatography on silica gel (MeOH/2 N NH_4Cl solution/MeCN, 7:2:1), extracted twice with chloroform, washed with 5 ml of a Na_2CO_3 solution (20%), and dried with $MgSO_4$. The solvent was evaporated, and the light brown viscous oil was dried in vacuo to yield 266 mg (63%) of **2c**. – IR (KBr): $\tilde{\nu}$ = 3422 cm^{-1} (OH), 3088 (CH aromat.), 2869 (CH aliphat.), 1609, 1565, 1515 (CC aromat.), 1112 (CO). – ^1H NMR ($CDCl_3$): δ = 3.19–3.71 (m, 48H, CH_2), 7.28 (d, *J* = 5.2 Hz, 2H, 3,8-H), 8.07 (s, 2H, 5,6-H), 8.93 (d, *J* = 5.2 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 53.2 (t, C-2′,2″,18′,18″), 69.2 (t, C-3′,3″,17′,17″), 70.5 (t, C-5′,5″,15′,15″), 70.8 (t, C-6′,6″,14′,14″), 70.9 (t, C-8′,8″,9′,9″,11′,11″,12′,12″), 113.6 (d, C-3,8), 121.1 (d, C-5,6), 123.7 (s, C-4a,6a), 148.5 (s, C-1a,10a), 149.8 (d, C-2,9), 155.9 (s, C-4,7).

4,7-Dipiperidino-1,10-phenanthroline (**2d**): Phenanthroline **1** (0.30 g, 1.20 mmol) and piperidine (5.00 g, 58.7 mmol) were heated at reflux for 24 h, then excess piperidine was distilled off from the deep brown solution. The residue was dissolved in 20 ml of chloroform and the solution washed twice with 10 ml of water. After drying with $MgSO_4$ the solvent was evaporated and the residue recrystallized from light petroleum ether (boiling range 60–70°C) to yield 0.30 g (72%) of **2d** as a light brown solid; m.p. 180°C. – IR (KBr): $\tilde{\nu}$ = 2919 cm^{-1} (CH), 2839 (CH), 2804 (NCH_2), 1608, 1567, 1514 (CC aromat.). – ^1H NMR ($CDCl_3$): δ = 1.69–1.77 (m, 4H, 4′,4″-H), 1.86–1.96 (m, 8H, 3′,3″,5′,5″-H), 3.19–3.26 (m, 8H, 2′,2″,6′,6″-H), 7.06 (d, *J* = 6.0 Hz, 2H, 3,8-H), 7.93 (s, 2H, 5,6-H), 8.93 (d, *J* = 6.0 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 24.4 (t, C-4′,4″) 26.2 (t, C-3′,3″,5′,5″), 53.7 (t, C-2′,2″,6′,6″), 110.8 (d, C-3,8), 120.8 (d, C-5,6), 123.1 (s, C-4a,6a), 148.1 (s, C-1a,10a), 150.4 (d, C-2,9), 158.0 (s, C-4,7). – MS (70 eV), *m/z* (%): 347 (24), 346 (100) [M^+], 345 (39), 317 (18), 303 (6), 291 (7), 290 (12), 289 (12), 263 (20), 233 (9), 206 (8), 179 (6), 178 (6), 173 (8), 117 (7), 41 (9). – HRMS calcd. for $C_{22}H_{26}N_4$ [M^+] 346.2158; found 346.2153. – $C_{22}H_{26}N_4$ (346.5): calcd. C 76.27, H 7.56, N 16.17; found C 76.11, H 7.62, N 15.98.

4,7-Dimorpholino-1,10-phenanthroline (**2e**): A mixture of **1** (0.40 g, 1.60 mmol) and morpholine (4.20 g, 48.2 mmol) was heated at reflux for 19 h. After evaporation of excess morpholine the brown slurry was dissolved in 20 ml of dichloromethane and the solution extracted five times with water. The combined organic layers were dried with $MgSO_4$, the solvent was evaporated in vacuo and the residue recrystallized from toluene to yield 0.42 g (75%) of a light brown solid; m.p. 247–249°C. – IR (KBr): $\tilde{\nu}$ = 3028 cm^{-1} (CH aromat.), 2957, 2938, 2867, 2832 (CH), 2812 (NCH_2), 1612, 1567, 1513 (CC aromat.), 1124 (CO). – ^1H NMR ($CDCl_3$): δ = 3.28 (t, *J* = 5.5 Hz, 8H, 2′,2″,6′,6″-H), 4.03 (t, *J* = 5.5 Hz, 8H, 3′,3″,5′,5″-H), 7.11 (d, *J* = 6.0 Hz, 2H, 3,8-H), 7.99 (s, 2H, 5,6-H), 9.02 (d, *J* = 6.0 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 52.7 (t, C-2′,2″,6′,6″), 67.0 (t, C-3′,3″,5′,5″), 111.0 (d, C-3,8), 120.8 (d, C-5,6), 122.8 (s, C-4a,6a), 148.2 (s, C-1a,10a), 150.7 (d, C-2,9), 156.7 (s, C-4,7). – MS (70 eV), *m/z* (%): 351 (24), 350 (100) [M^+], 349 (9), 319 (7), 293 (14), 292 (52), 291 (13), 262 (9), 261 (11), 247 (8), 235 (17), 234 (68), 233 (58), 207 (11), 206 (24), 205 (13), 180 (11), 179 (18), 178 (16), 151 (9), 103 (24), 102 (8), 90 (18). – HRMS: calcd. for $C_{22}H_{26}N_4O_2$ [M^+] 350.1743; found 350.1745. – $C_{22}H_{26}N_4O_2 \cdot 0.5\ H_2O$ (359.4): calcd. C 66.84, H 6.45, N 15.59; found C 66.50, H 6.33, N 15.68.

4,7-Bis(4-methyl-1-piperazinyl)-1,10-phenanthroline (**2f**): Phenanthroline **1** (0.50 g, 2.00 mmol) and 1-methylpiperazine (6.00 g, 60.0 mmol) were heated at reflux for 5 h, then the remaining 1-methylpiperazine was evaporated. The deep brown mixture was dissolved in 2 N NaOH and the solution extracted five times with dichloromethane. After drying with $MgSO_4$ the solvent was evaporated and the residue recrystallized from toluene to afford 0.51 g (69%) of light brown crystals; m.p. 165°C. – IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1} (CH), 2930 (CH), 2838, 2800, 2787, (NCH_2), 1613, 1570, 1511 (CC aromat.). – ^1H NMR ($CDCl_3$): δ = 2.45 (s, 6H, CH_3), 2.71–2.79 (m, 8H, 2′,2″,6′,6″-H), 3.26–3.36 (m, 8H, 3′,3″,5′,5″-H), 7.10 (d, *J* = 6.0 Hz, 2H, 3,8-H), 7.97 (s, 2H, 5-H), 8.99 (d, *J* = 6.0 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 46.2 (q, Me), 52.2 (t, C-3′,3″,5′,5″), 55.2 (t, C-2′,2″,6′,6″), 111.1 (d, C-3,8), 120.8 (d, C-5,6), 122.9 (s, C-4a,6a), 148.1 (s, C-1a,10a), 150.6 (d, C-2,9), 156.9 (s, C-4,7). – MS (70 eV), *m/z* (%): 377 (7), 376 (28) [M^+], 361 (4), 307 (5), 306 (16), 294 (8), 233 (5), 71 (40), 70 (79), 58 (11), 57 (6), 56 (7), 44 (6), 43 (100), 42 (39). – HRMS calcd. for $C_{22}H_{28}N_6$ [M^+] 376.2375; found 376.2373. – $C_{22}H_{28}N_6 \cdot 0.25\ H_2O$ (381.0): calcd. C 69.35, H 7.54, N 22.06; found C 69.39, H 7.26, N 22.06.

4,7-Bis(isopropylthio)-1,10-phenanthroline (**2g**): A mixture of 2-propanethiol (1.00 ml, 10.0 mmol), **1** (250 mg, 1.00 mol), and 800 mg of Na_2CO_3 in 10 ml of dry acetonitrile was stirred in a high-pressure tube at 150°C for 75 min. After cooling to room temp. the solvent was evaporated. The colorless residue was dissolved in

25 ml of water/25 ml of dichloromethane. The organic layer was separated, dried with $MgSO_4$, and concentrated to a small volume. After addition of pentane colorless **2g** precipitated in ca. 12 h, which was filtered off and dried in vacuo to furnish 154 mg (47%) of **2g**; m.p. 152°C. – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 3015 (CH aromat.), 2963, 2922, 2864 (CH aliphat.), 1606, 1546, 1492, 1410 (CC aromat.). – ^1H NMR ($CDCl_3$): δ = 1.48 (d, *J* = 6.6 Hz, 12H, 1′,1″,3′,3″-H), 3.72 (sept, *J* = 6.6 Hz, 2H, 2′,2″-H), 7.47 (d, *J* = 4.9 Hz, 2H, 3,8-H), 8.18 (s, 2H, 5,6-H), 8.97 (d, *J* = 4.9 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 22.8 (q, C-1′,1″,3′,3″), 36.4 (d, C-2′,2″), 120.4 (d, C-3,8), 122.2 (d, C-5,6), 127.3 (s, C-4a,6a), 146.0 (s, C-1a,10a), 146.9 (s, C-4,7), 149.2 (d, C-2,9). – $C_{18}H_{20}N_2S_2$ (328.5): calcd. C 65.82, H 6.14, N 8.53; found C 66.12, H 5.72, N 8.14.

4,7-Bis(4-methylphenylthio)-1,10-phenanthroline (**2h**): A mixture of 4-methylthiophenol (150 mg, 1.20 mmol), **1** (100 mg, 0.400 mol), and 500 mg of Na_2CO_3 in 10 ml of dry acetonitrile was stirred in a high-pressure tube at 150°C for 2 h. After cooling to room temp. the solvent was evaporated. The colorless residue was dissolved in 25 ml of water/25 ml of dichloromethane. The organic layer was separated, dried with $MgSO_4$ and concentrated to a small volume. After addition of pentane colorless crystals precipitated, which were filtered off and dried in vacuo to yield 137 mg (80%) of **2h**; m.p. 200°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3018 cm^{-1} (CH aromat.), 2914 (CH aliphat.), 1599, 1546, 1490, 1410 (CC aromat.). – ^1H NMR ($CDCl_3$): δ = 2.45 (s, 6H, Me), 6.95 (d, *J* = 4.9 Hz, 2H, 3,8-H), 7.32 (d, *J* = 8.4 Hz, 4H, 3′,3″,5′,5″-H), 7.53 (d, *J* = 8.1 Hz, 4H, 2′,2″,6′,6″-H), 8.26 (s, 2H, 5,6-H), 8.81 (d, *J* = 4.9 Hz, 2H, 2,9-H). – ^{13}C NMR ($CDCl_3$): δ = 21.6 (q, Me), 120.0 (d, C-3,8), 122.1 (d, C-5,6), 126.1 (s, C-4a,6a), 126.2 (s, C-4′,4″), 131.2 (d, C-3′,3″,5′,5″), 135.7 (d, C-2′,2″,6′,6″), 140.6 (s, C-1′,1″), 149.6 (s, C-4,7,1a,10a), 149.7 (d, C-2,9). – $C_{26}H_{20}N_2S_2$ (424.6): calcd. C 73.55, H 4.75, N 6.60; found C 73.34, H 4.59, N 6.26.

General Procedure for the Preparation of the Tris[4,7-bis(aza-crown ether)-1,10-phenanthroline]iron(II) Hexafluorophosphates **3a–c**: A mixture of 0.250 mmol of a 4,7-bis(aza-crown ether)-1,10-phenanthroline **2a–c** and 0.090 mmol of iron(II) sulfate heptahydrate was stirred under nitrogen in 5 ml of distilled water at room temp. until a deep red solution had formed. After addition of 0.20 mmol of potassium perchlorate (for **3a**), potassium hexafluorophosphate (for **3b**), or caesium hexafluorophosphate (for **3c**) a deep red product precipitated. The red solid was filtered off, washed with 20 ml of distilled water, and dried in vacuo.

Tris[4,7-bis(4,7,10-trioxa-1-azacyclododecyl)-1,10-phenanthroline]iron(II) Perchlorate (**3a**): Yield 63%, red solid; m.p. >220°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (CH aromat.), 2912, 2865 (CH aliphat.), 1595, 1551, 1507 (CC aromat.), 1121 (CO), 1089 (ClO). – UV (CH_3CN): λ_{max} (lg ε) = 544 nm (4.33). – ^1H NMR ($CDCl_3$): δ = 3.70 (br. s, 48H, 5′,6′,8′,9′-H), 3.79 (br. s, 24H, 3′,11′-H), 3.90 (br. s, 24H, 2′,12′-H), 6.97 (d, *J* = 6.0 Hz, 6H, 3,8-H), 7.30 (d, *J* = 6.0 Hz, 6H, 2,9-H), 8.65 (s, 6H, 5,6-H). – ^{13}C NMR ($CDCl_3$): δ = 53.6 (t, C-2′,12″), 68.7 (t, C-3′,11′), 70.8 (t, C-5′,9′), 71.0 (t, C-6′,8′), 111.7 (d, C-3,8), 122.3 (d, C-5,6), 123.5 (s, C-4a,6a), 151.8 (s, C-1a,10a), 153.1 (d, C-2,9), 154.6 (s, C-4,7). – $E^{ox}_{1/2}$ = 0.01 V. – $C_{84}H_{114}Cl_2FeN_{12}O_{26}$ (1834.7): calcd. C 54.99, H 6.26, N 9.16; found C 54.64, H 6.27, N 9.03.

Tris[4,7-bis(4,7,10,13-tetraoxa-1-azacyclopentyl)-1,10-phenanthroline]iron(II) Hexafluorophosphate (**3b**): Yield 34%, red solid; m.p. 96–98°C. – IR (KBr): $\tilde{\nu}$ = 3087 cm^{-1} (CH aromat.), 2864 (CH aliphat.), 1596, 1552, 1508 (CC aromat), 1121 (CO), 841 (PF). – UV (MeCN): λ_{max} (lg ε) = 543 nm (4.30). – ^1H NMR (CD_3CN): δ = 3.53–3.55 (m, 72H, 5′,6′,8′,9′,11′,12′-H), 3.78–3.80 (m, 48H, 2′,3′,14′,15′-H), 7.04 (d, *J* = 6.1 Hz, 6H, 3,8-H), 7.27 (d, *J* = 6.1 Hz, 6H, 2,9-H), 8.35 (s, 6H, 5,6-H). – ^{13}C NMR (CD_3CN): δ = 54.1 (t, C-2′,15′), 69.7 (t, C-3′,14′), 70.4 (t, C-5′,12′), 70.8 (t, C-6′,11′), 71.1 (t, C-8′,9′), 113.0 (d, C-3,8), 122.6 (d, C-5,6), 124.1 (s, C-4a,6a), 152.3 (s, C-1a,10a), 153.3 (d, C-2,9), 156.2 (s, C-4,7). – $E^{ox}_{1/2}$ = 0.04 V. – $C_{96}H_{138}F_{12}FeN_{12}O_{24}P_2 \cdot 4\,H_2O$ (2262.1): calcd. C 50.97, H 6.51, N 7.43; found C 50.97, H 6.40, N 7.25.

Tris[4,7-bis(4,7,10,13,16-pentaoxa-1-azacyclooctadecyl)-1,10-phenanthroline]iron(II) Hexafluorophosphate (**3c**): Yield 64%, m.p. 102°C. – IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (CH aromat.), 2871 (CH aliphat.), 1617, 1596, 1554 (CC aromat.), 1117 (CO), 842 (PF). – UV (CH_3CN): λ_{max} (lg ε) = 543 nm (4.37). – ^1H NMR (CD_3CN): δ = 3.19–3.46 (m, 96H, 5′,6′,8′,9′,11′,12′,14′,15′-H), 3.60–3.72 (m, 48H, 2′,3′,17′,18′-H), 7.21 (d, *J* = 6.0 Hz, 6H, 3,8-H), 7.39 (d, *J* = 6.0 Hz, 6H, 2,9-H), 8.20 (s, 6H, 5,6-H). – ^{13}C NMR (CD_3CN): δ = 53.5 (t, C-2′,18′), 68.8 (t, C-3′,17′), 70.7 (t, C-5′,6′,8′,9′,11′,12′,14′,15′), 115.2 (d, C-3,8), 122.7 (d, C-5,6), 124.5 (s, C-4a,6a), 152.2 (s, C-1a,10a), 153.6 (d, C-2,9), 156.9 (s, C-4,7). – $E^{ox}_{1/2}$ = 0.08 V. – $C_{108}H_{162}F_{12}FeN_{12}O_{30}P_2 \cdot 0.5\,CsPF_6$ (2593.2): calcd. C 50.02, H 6.30, N6.48; found C 49.88, H 6.18, N 6.11.

General Procedure for the Preparation of the Tris(4,7-diamino-1,10-phenanthroline)iron(II) Hexafluorophosphates **3d–f**: To a solution of 0.118 mmol of the 4,7-diamino-1,10-phenanthroline (**2d–f**) in 2.0 ml of distilled water and 1.0 ml of methanol was added a solution of 10.8 mg (0.039 mmol) of iron(II) sulfate heptahydrate in 1.4 ml of distilled water. The deep red, clear solution was sonicated with ultrasound for 10 min, and a solution of 12.9 mg (0.079 mmol) of ammonium hexafluorophosphate in 161 µl of distilled water was added dropwise. Subsequently, the deep red solid was filtered off, washed three times with distilled water by centrifugation techniques and dried at 80°C in vacuo.

Tris(4,7-dipiperidino-1,10-phenanthroline)iron(II) Hexafluorophosphate (**3d**): Yield 70%, m.p. 236–239°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2909 cm^{-1} (CH), 2829 (CH), 2809 (NCH_2), 1615, 1595, 1551 (CC aromat.), 849 (PF). – UV (CH_3CN): λ_{max} (lg ε) = 526 nm (3.29), 505 (3.28). – ^1H NMR ($CDCl_3$): δ = 1.69–1.79 (m, 12H, 4′-H), 1.79–1.89 (m, 24H, 3′,5′-H), 3.30–3.41 (m, 24H, 2′,6′-H), 7.03 (d, *J* = 7.0 Hz, 6H, 3,8-H), 7.40 (d, *J* = 7.0 Hz, 6H, 2,9-H), 7.90 (s, 6H, 5,6-H). – ^{13}C NMR ($CDCl_3$): δ = 24.1 (t, C-4′,4″), 25.9 (t, C-3′,3″,5′,5″), 53.1 (t, C-2′,2″,6′,6″), 113.5 (d, C-3,8), 122.0 (d, C-5,6) 123.9 (s, C-4a,6a), 151.2 (s, C-1a,10a), 154.5 (d, C-2,9), 157.3 (s, C-4,7). – $E^{ox}_{1/2}$ = 0.13 V. – $C_{66}H_{78}F_{12}FeN_{12}P_2 \cdot H_2O$ (1403.3): calcd. C 56.49, H 5.75, N 11.98; found C 56.57, H 5.73, N 11.58.

Tris(4,7-dimorpholino-1,10-phenanthroline)iron(II) Hexafluorophosphate (**3e**): Yield 83%, m.p. 272–275°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1}, 2899, 2869 (CH), 1617, 1594, 1557 (CC aromat.), 1117 (CO), 847 (PF). – UV (CH_3CN): λ_{max} (lg ε) = 522 nm (4.35), 500 (4.34). – ^1H NMR ($CDCl_3/CD_3OD$): δ = 3.19–3.26 (m, 24H, 2′,6′-H), 3.72–3.80 (m, 24H, 3′,5′-H), 6.85 (d, *J* = 6.0 Hz, 6H, 3,8-H), 7.21 (d, *J* = 6.0 Hz, 6H, 2,9-H), 7.87 (s, 6H, 5,6-H). – ^{13}C NMR (CD_3CN): δ = 53.0 (t, C-2′,2″,6′,6″), 67.1 (t, C-3′,3″,5′,5″), 113.9 (d, C-3,8), 123.5 (d, C-5,6), 125.0 (s, C-4a,6a), 152.1 (s, C-1a,10a), 155.6 (d, C-2,9), 157.9 (s, C-4,7). – $E^{ox}_{1/2}$ = 0.22 V. – $C_{60}H_{66}FeN_{12}O_6(PF_6)_{2.4}$ (1455.1): calcd. C 49.53, H 4.57, N 11.55; found C 49.52, H 4.64, N 11.45.

Tris[4,7-bis(4-methyl-1-piperazinyl)-1,10-phenanthroline]iron(II) Hexafluorophosphate (**3f**): Yield 77%, m.p. 238–241°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2925, 2850 cm^{-1} (CH), 2790 (NCH_2), 1620, 1600, 1558 (CC aromat.), 850 (PF). – UV (CH_3CN): λ_{max} (lg ε) = 525 nm (4.21), 505 (4.20). – ^1H NMR

($CDCl_3/CD_3OD$): δ = 2.36 (s, 18H, Me), 2.63–2.73 (m, 24H, 3′,5′-H), 3.33–3.43 (m, 24H, 2′,6′-H), 6.97 (d, J = 7.0 Hz, 6H, 3,8-H), 7.31 (d, J = 7.0 Hz, 6H, 2,9-H), 7.93 (s, 6H, 5,6-H). – ^{13}C NMR ($CDCl_3/CD_3CN$): δ = 46.1 (q, Me), 51.8 (t, C-3′,3″,5′,5″), 54.8 (t, C-2′,2″,6′,6″), 114.0 (d, C-3,8), 122.2 (d, C-5,6), 124.0 (s, C-4a,6a), 151.3 (s, C-1a,10a), 155.2 (d, C-2,9), 156.6 (s, C-4,7). – $E^{ox}_{1/2}$ = 0.23 V. – $C_{66}H_{84}F_{12}FeN_{18}P_2 \cdot 5\ H_2O$ (1565.4): calcd. C 50.64, H 6.05, N 16.11; found C 50.60, H 5.55, N 15.74.

General Procedure for the Preparation of the Tris[4,7-bis(alkyl- or arylthio) -1,10-phenanthroline]iron(II) Hexafluorophosphates **3g,h**: 0.457 mmol of **2g** or **h** was dissolved in 3 ml of chloroform and 3 ml of acetone. Then a solution of iron(II) sulfate heptahydrate (0.167 mmol) in 10 ml of distilled water was added, and the mixture was stirred at room temp. for about 30 min. A deep red solution formed, from which **3g,h** precipitated after addition of 0.300 mmol of ammonium hexafluorophosphate. The red solid was filtered off, washed with 20 ml of distilled water, and dried in vacuo.

Tris[4,7-bis(isopropylthio)-1,10-phenanthroline]iron(II) Hexafluorophosphate (**3g**): Yield 91%, m.p. >240°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2973 cm^{-1}, 2927, 2866 (CH), 1617, 1586, 1544 (CC aromat.), 845 (PF). – UV (CH_3CN): λ_{max} (lg ε) = 538 nm (4.22). – ^1H NMR ($CDCl_3$): δ = 1.43 (d, J = 6.6 Hz, 18H, 1′-H), 1.55 (d, J = 6.6 Hz, 18H, 3′-H), 3.75 (sept, J = 6.6 Hz, 6H, 2′-H), 7.47 (d, J = 5.6 Hz, 6H, 3,8-H), 7.57 (d, J = 5.6 Hz, 6H, 2,9-H), 8.19 (s, 6H, 5,6-H). – ^{13}C NMR ($CDCl_3$): δ = 22.6 (q, C-1′), 22.7 (q, C-3′), 36.4 (d, C-2′), 121.3 (d, C-3,8), 123.0 (d, C-5,6), 127.9 (s, C-4a,6a), 148.4 (s, C-1a,10a), 151.0 (s, C-4,7), 154.7 (d, C-2,9). – $E^{ox}_{1/2}$ = 0.56 V. – $C_{54}H_{60}F_{12}FeN_6P_2S_6 \cdot 2\ H_2O$ (1361.25): calcd. C 47.44, H 4.72, N 6.15, S 14.07; found C 47.31, H 4.70, N 5.67, S 13.44.

Tris[4,7-bis(4-methylphenylthio)-1,10-phenanthroline]iron(II) Hexafluorophosphate (**3h**): Yield 77%, m.p. >240°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} (CH), 1618, 1585, 1545 (CC aromat.), 838 (PF). – UV (CH_3CN): λ_{max} (lg ε) = 543 nm (4.35). – ^1H NMR ($CDCl_3$): δ = 2.38 (s, 18H, Me), 6.90 (d, J = 5.5 Hz, 6H, 3,8-H), 7.25 (d, J = 5.5 Hz, 6H, 2,9-H), 7.29 (d, J = 7.6 Hz, 12H, 3′,5′-H), 7.46 (d, J = 7.6 Hz, 12H, 1′,6′-H), 8.26 (s, 6H, 5,6-H). – ^{13}C NMR (CD_3CN): δ = 21.6 (q, Me), 121.5 (d, C-3,8), 123.7 (d, C-5,6), 127.9 (s, C-4a,6a), 131.1 (d, C-2′,3′,5′,6′), 136.1 (s, C-4′), 142.4 (s, C-1′), 149.0 (s, C-1a,10a), 153.4 (s, C-4,7), 154.9 (d, C-2,9). – $E^{ox}_{1/2}$ = 0.61 V. – $C_{78}H_{60}F_{12}FeN_6P_2S_6 \cdot 3\ H_2O$ (1673.6): calcd. C 55.45, H 3.94, N 4.97, S 11.39; found C 55.86, H 3.99, N 4.92, S 10.61.

[1] New Materials for Sensors, part 3; for part 2 see ref.[17].

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