Supporting Information

SYNTHESIS AND MESOMORPHIC PROPERTIES OF IRON (II) CONTAINING DENDRIMERIC COMPLEXES DERIVATIVE OF 3,4-*n*-DODECYLOXYBENZOYL POLY(PROPYLENE IMINE)

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The yield of iron compounds and conditions of synthesis are presented in Table S1.

Table S1. Conditions of synthesis iron containing complexes of dendrimers from the 1st to 5th generations

Complexes	Reagents, [mg] [mmol]	Solvent, V [ml]	T [°C]	τ, hours	yield, [%]	atmosphere
1-K2.10- (FeCl₂)₃	1-K2.10L, 200 (0.1) FeCl ₂ , 127 (0.001)	THF, 37	23	18	78.7	Ar
2-K2.10- (FeCl₂)₆	2-K2.10L, 200 (0.049) FeCl ₂ , 137 (0.001)	THF, 40	23	22	58.3	Ar
3-K2.10- (FeCl₂)_{14.6}	3-K2.10L, 400 (0.048) FeCl ₂ , 255.53 (0.0021)	THF, 48	23	26	78.2	Ar
4-K2.10- (FeCl₂)₂₁	4-K2.10L, 200 (0.012) FeCl ₂ , 128 (0.001)	THF, 52	23	30	69.4	Ar
5-K2.10- (FeCl₂)_{106.5}	5-K2.10L, 200 (0.006) FeCl ₂ , 130 (0.00101)	THF, 56	23	32	68.7	Ar

The purity of the complexes has been checked by size exclusion chromatography (SEC), Fig. S1.

Figure S1. SEC chromatogram of the free 2-K2.10 ligand (b) and the complex 2K2.10-(FeCl₂)₆ (a).

Table S2. Data of GPC-analysis complexes of dendrimers from the 1st to 5th generations

Серия I.	Mn, g/mol		Mw, g/mol		Vp, мл		Mp, g/mol	
	UV	IR	UV	IR	UV	IR	UV	IR
1	3.97·10 ³	1.63·10 ³	6.86·10 ³	4.97·10 ³	21.26	21.24	7.24·10 ³	7.28·10 ³
2	1.51·10 ⁴	1.73·10 ⁴	1.89·10 ⁴	1.94·10 ⁴	19.8	19.8	1.88·10 ⁴	1.89·10 ⁴
3	5.12·10 ³	1.76·10 ³	2.7·10 ⁴	1.75·10 ⁴	19.1	19.1	3.16·10 ⁴	3.16·10 ⁴
4	4.08·10 ⁴	3.69·10 ⁴	5.22·10 ⁴	5.47·10 ⁴	18.4	18.4	4.55·10 ⁴	4.55·10 ⁴
5	8.85·10 ³	2.45·10 ³	5.21·10 ⁴	4.03·10 ⁴	17.9	17.9	6.27·10 ⁴	6.23·10 ⁴

Vp – volume of solvent

The elution volume and Mp index of the complexes is considerably different from that of the free ligands as shown exemplarily in Fig. S2.

Figure S2. Relation M_p from generation of ligands and complexes.

The elemental analysis (EA) revealed the following iron content for the complexes of each generation:

Table S3. Elemental analysis of the Fe^{II} complexes

	Compounds	C%	H%	N%	O%	Fe%	Cl%
1	C ₁₂₄ H ₂₁₆ N ₆ O ₁₂ Fe ₃ Cl ₆	62.60 (61.94)	9.8 (9.05)	3.53 (3.7)	8.07 (8.85)	7.04 (6.97)	8.95 (9.49)
2	C ₂₅₆ H ₄₄₈ N ₁₄ O ₂₄ Fe ₁₂ Cl ₆	62.76 (59.22)	9.87 (8.49)	4 (3.88)	7.84 (12.04)	6.84 (6.7)	8.94 (9.67)
3	C ₅₂₀ H ₉₁₂ N ₃₀ O ₄₈ Fe ₁₅ Cl ₃₀	60.85 (59.01)	9.59 (8.77)	4.09 (4.07)	7.48 (10.6)	7.92 (7.68)	10.06 (9.87)
4	C ₁₀₄₈ H ₁₈₄₀ N ₆₂ O ₉₆ Fe ₂₂ Cl ₄₄	63.7 (59.5)	10.05 (9.02)	4.39 (4.5)	7.77 (10.65)	6.21 (5.84)	7.9 (10.49)
5	C ₂₁₀₄ H ₃₆₉₆ N ₁₂₆ O ₁₉₂ Fe ₁₀₆ Cl ₂₁₃	53.08 (51.82)	8.38 (7.88)	3.71 (4.42)	6.45 (10.7)	12.5 (12.1)	15.87 (12.98)

Remark: (*) experimental data.

From the EA data, the number of iron atoms $n_{EA}(Fe)$ with respect to the number of C atoms $n(C)$ in the perfectly built dendrimeric molecule can be calculated according to:

$$\frac{n_{EA}(Fe)}{n(C)} = \frac{w_{EA}(Fe)}{M(Fe)} \cdot \frac{M(C)}{w_{EA}(C)}$$

$w_{EA}(Fe)$, $w_{EA}(C)$ are the weight fractions from EA, $M(Fe)$ and $M(C)$ are the molar masses of Fe and C atoms.

The fractional number of iron atoms in 3-K2.10-(FeCl₂)_{14.6} and 5-K2.10-(FeCl₂)_{106.5} may reflect by several reason: a) a certain distribution of coordinated iron sites in the dendrimeric ligand, b) the presence of different coordination numbers and geometries in one and the same complex (as it was found for analogous copper complexes [17]) and c) the real existing defect structures in the dendrimeric ligands.

In the MALDI-TOF spectrum of 1-K2.10-(FeCl₂)₃, we observe - beside a peak of the free ligand - complexes with one and with two iron atoms per dendrimer. EA revealed that most of the sample should consist of the complex with two iron centres. With respect to the MALDI results, the iron content revealed by EA must be regarded as a mean value, indicating a certain distribution of the number of iron sites in the dendrimeric complex molecules. For 2-K2.10-(FeCl₃)₆, we observe analogous results, Fig. S3. In MALDI-TOF, the whole series from one up to a four iron centres in a PPI dendrimer ligand can be observed.

Figure S3. Mass-spectrum of 2L-(FeCl₃)₆, matrix 7-hydroxycoumarin.

Peaks with higher iron content cannot be detected; they would have a too small intensity. Results of MALDI-TOF experiments presents in Table S4.

Table S4. Data of MALDI-TOF experiments

Compound	molecular weight	
	computed value*	found value **
1-K2.10-(FeCl₂)₃	1983.12 [L] *	1984.91 [M ⁺ L +1] **
	2038.97 [L•Fe]	2042.29 [M ⁺ L•Fe +4]
	2061.96 [L•Na•Fe]	2061.71 [M ⁺ L•Na•Fe -2]
	2078.05 [M ⁺ L• K•Fe]	2074.61 [M ⁺ L• K•Fe-4]
	2084.95 [M ⁺ L•2Na•Fe]	2089.63 [M ⁺ L•2Na•Fe +5]
	2107.94 [M ⁺ L•3Na•Fe]	2109.77 [M ⁺ L•3Na•Fe +2]
	2140.81 [M ⁺ L•2Na•2Fe]	2144.35 [M ⁺ L•2Na•2Fe +4]
	2163.79 [M ⁺ L•3Na•2Fe]	2168.59 [M ⁺ L•3Na•2Fe +5]
	2196.65 [M ⁺ L•2Na•3Fe]	2201.91 [M ⁺ L•2Na•3Fe +5]
2-K2.10-(FeCl₂)₆	4106.47 [L]	4105.89 [M ⁺ L -1]
	4162.32 [L•Fe]	4166.6 [M ⁺ L•Fe +4]
	4185.31 [L•Na•Fe]	4183.56 [M ⁺ L•Na•Fe -2]
	4201.42 [L•K•Fe]	4200.03 [M ⁺ L•K•Fe -1]
	4218.17 [L•2Fe]	4221.8 [M ⁺ L•2Fe +3]
	4241.16 [L•Na•2Fe]	4238.13 [M ⁺ L•Na•2Fe -3]
	4257.27 [L•K•2Fe]	4257.24 [M ⁺ L•K•2Fe]
	4274.02 [L•3Fe]	4277.39 [M ⁺ L•3Fe +3]
	4329.87 [L•4Fe]	4327.2 [M ⁺ L•4Fe -2]
	4385.72 [L•5Fe]	4385.32 [M ⁺ L•5Fe]
3-K2.10-(FeCl₂)_{14.55}	8353.1 [L]	8354.6 [M ⁺ L +1]
	8408.95 [L•Fe]	8407.68 [M ⁺ L•Fe -1]
	8431.94 [M ⁺ L•Na•Fe]	8433.94 [M ⁺ L•Na•Fe+2]
4-K2.10-(FeCl₂)₂₂	16846.59 [L]	16847.41 [M ⁺ L +1]
5-K2.10-(FeCl₂)_{106.5}	–	–

Remark: * ligand – [L] and amount of iron ions – [L•Fe]; ** composition of experimental molecular ion [M⁺L +n] and amount of iron ions – [M⁺L•Fe+n], where n – difference between theoretical and experimental data.

Figure S4. DSC of **1-K2.10-(FeCl₂)₃** (1), 2-nd heating/cooling.

Figure S5. DSC of **2-K2.10-(FeCl₂)₆** (2), 2-nd heating/cooling.

Figure S6. DSC of **3-K2.10-(FeCl₂)_{14.6}** (**3**), 2-nd heating/cooling.

Figure S7. DSC of **4-K2.10-(FeCl₂)₂₁** (**4**), 2-nd heating/cooling.

Figure S8. DSC of **5-K2.10-(FeCl₂)_{106.5} (5)**, 2-nd heating/cooling.

Series of photographs of **2-K2.10 (FeCl₂)₆** showing the difference between the Colh phase and the crystalline phase was included into SI of manuscript.

Solid state of **2-K2.10 (FeCl₂)₆**, RT

Transition from «solid to mesophase» of **2-K2.10 (FeCl₂)₆** in the heating cycle at T=89°C.

Texture of **2-K2.10 (FeCl₂)₆** in the heating cycle at T=116.7°C.

Transition from «mesophase to Iso» of **2-K2.10 (FeCl₂)₆** in the heating cycle at T=180°C.

Transition from «Isotrope to mesophase» of **2-K2.10 (FeCl₂)₆** in cooling cycle at T=176°C.

Texture of **2-K2.10** (FeCl_2)₆ in cooling cycle at RT.