

Six-Membered Metalla-coronands. Synthesis and Crystal Packing: Columns, Compartments, and 3D-Networks^{†,‡}Rolf W. Saalfrank,^{*,§} Christian Deutscher,[§] Stefan Sperner,[§] Takayuki Nakajima,[§] Ayuk M. Ako,[§] Eveline Uller,[§] Frank Hampel,[§] and Frank W. Heinemann^{||}*Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany, and Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany*

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Reaction of various *N*-substituted diethanolamines H_2L^3 (**4**) with calcium hydride and iron(III) chloride leads to the self-assembly of six-membered ferric wheels $[Fe_6X_6(L^3)_6]$ (**5**). Principally, all the iron coronands are isostructural; however, they differ fundamentally with respect to their crystal packing. Exemplarily, this is discussed for selected members of the space groups $R\bar{3}$, $P\bar{3}$, $P2_1/c$, $P2_1/n$, $C2/c$, and $P\bar{1}$. Depending on the nature of their sidearms, the ferric wheels create various substructures. For instance, the ferric wheels **5a–i** of space group $R\bar{3}$ or $P\bar{3}$ are piled in parallel in cylindrical columns, which are surrounded by six parallel columns alternately dislocated by $1/3c$ and $2/3c$ against the central one. Pronounced van der Waals interactions give rise to compartmentation and incarceration of guest molecules as seen for **5e,g**. However, in **5h** strong π – π interactions create a three-dimensional scaffold. The most significant difference of the ferric wheels **5j–p** of space groups $P2_1/c$, $P2_1/n$, and $C2/c$ is that these ferric wheels are arranged in parallel in two orientations. They differ mainly only by the included angle of the two groups of parallel wheels. In the case of **5l**, molecular chains are formed in the crystal due to π – π interactions. The ferric wheels **5q–y** of space group $P\bar{1}$ are packed in the crystal most simply, with all the ferric wheels piled in parallel.

Introduction

Polyoxometalates have become the focus of intense research activities, because these compounds exhibit an enormous variety of structures as well as magnetic properties.¹ Over the past several years, considerable progress has been made toward the predictability of ordered supramolecular assemblies on the basis of coordinative metal/ligand

bonds.² A particular symmetric class are the so-called ferric wheels with 6, 8, 10, 12, and even 18 iron(III) ions.³ The magnetization of the ferric wheels exhibits steplike field dependencies at low temperatures and can be regarded as ideal model systems for so-called single molecule magnets (SMMs), the finite-size version of the linear Heisenberg chain.⁴ Since SMMs are promising new materials, this class of molecules becomes more and more important.

We reported on the template-mediated self-assembly of six- and eight-membered iron-coronates $\{Na[Fe_6(L^1)_6]\}^+$ (**1**) and $\{Cs[Fe_8(L^1)_8]\}^+$ (**2**).⁵ They were prepared from triethanolamine H_3L^1 with iron(III) chloride, sodium hydride, or cesium carbonate (Scheme 1). For instance, ferric wheel **1** allowed us to demonstrate the exciting effect of cooling by adiabatic magnetization.⁶

A common feature of complexes **1** and **2** is that the oxygen donors of one kind of ethanolate arm solely function as ligands for the coordinative saturation of the iron centers and for charge compensation, whereas the ethanolato μ_2 -O donors are structure determining. They are linkers, necessary for the ring formation. Consequently, reaction of *N*-methyl-di-

* To whom correspondence should be addressed. E-mail: saalfrank@chemie.uni-erlangen.de. Fax: (+49)9131-852-1165.

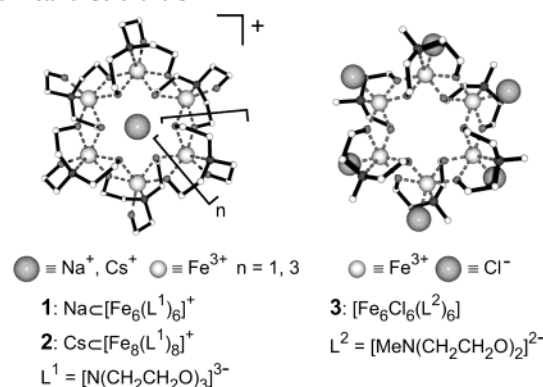
[†] Dedicated to Professor Fritz Vögtle on the occasion of his 65th birthday.

[‡] Chelate complexes (metalla-coronands). 27. Part 26: see ref 9.

[§] Institut für Organische Chemie der Universität Erlangen-Nürnberg.

^{||} Institut für Anorganische Chemie der Universität Erlangen-Nürnberg.

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Scheme 1. Schematic Representation of the Metalla-Coronates **1** and **2** and Metalla-Coronand **3**

ethanolamine H_2L^2 with calcium hydride and iron(III) chloride yielded the unoccupied neutral iron-coronand $[\text{Fe}_6\text{Cl}_6(\text{L}^2)_6]$ (**3**).⁷ Like in **1** and **2**, the $\mu_2\text{-O}$ donors of the *N*-methyl-diethanolamine ligands in **3** are structure determining. Completion of the octahedral coordination sphere at iron and charge compensation is achieved by the chloride co-

ligands (Scheme 1). Consequently, this new synthesis for six-membered ferric wheels was applied for the convergent synthesis of metallo-dendrimers.⁸ Variable temperature NMR spectroscopy, exemplarily carried out on a diamagnetic indium analogue, revealed that these species are not rigid and undergo nondissociative topomerization processes.⁹

A precondition for a crystal to behave like a ferromagnetic particle is the alignment of all magnetic moments and a minimum of intermolecular interactions. Therefore, it is decisive to control the crystal packing.¹⁰

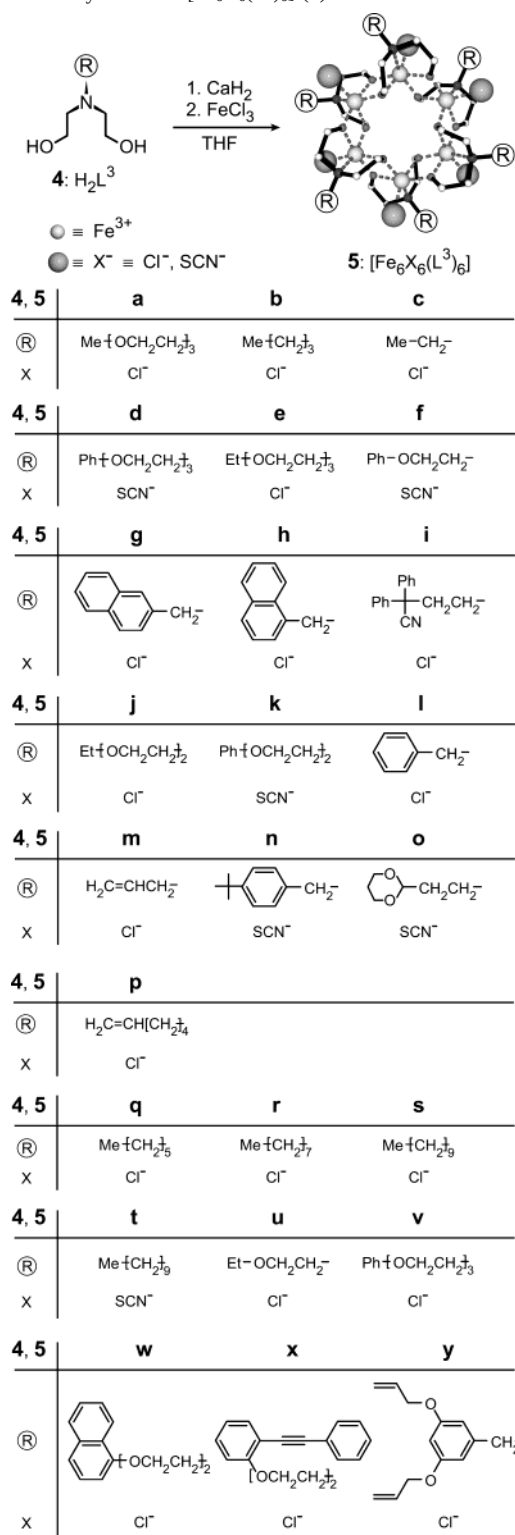
An additional interesting feature of oligonuclear assemblies is their readiness to frame compartments and three-dimensional networks with discrete channels and pores.^{10–12}

Results and Discussion

Herein we report on the crystal packing of several six-membered ferric wheels $[\text{Fe}_6\text{X}_6(\text{L}^3)_6]$ (**5**), generated from various *N*-substituted diethanolamines H_2L^3 (**4**), calcium hydride, and iron(III) chloride (Scheme 2).

The focal point of the present manuscript is to gain insights to which extent the crystal packing of basically similar molecules can be controlled by variation of their periphery

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Scheme 2. Synthesis of $[\text{Fe}_6\text{X}_6(\text{L}^3)_6]$ (**5**)

by means of different substituents. In order to classify the numerous structures, space groups were applied.

For an unambiguous characterization, we carried out X-ray crystallographic structure analyses of **5** (Table 1).^{13,14} Prin-

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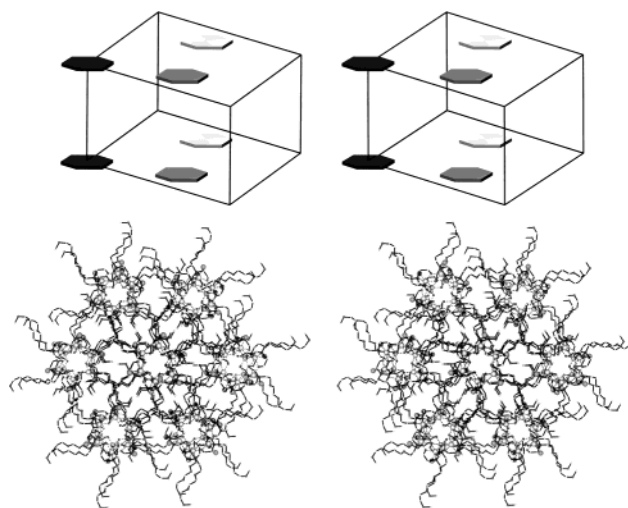


Figure 1. Top: stereo presentation of the crystal packing of **5a–h**. Bottom: stereoview of the crystal packing of the ferric wheel **5a**. View along the *c*-axis. Solvent molecules omitted for clarity.

cipally, all the six-membered ferric wheels $[\text{Fe}_6\text{X}_6(\text{L}^3)_6]$ (**5**) are isostructural with iron-coronand $[\text{Fe}_6\text{Cl}_6(\text{L}^2)_6]$ (**3**); however, there are fundamental differences concerning their crystal packing. Exemplarily, this will be discussed for selected members of the space groups $R\bar{3}$, $P\bar{3}$, $P2_1/c$, $P2_1/n$, $C2/c$, and $P\bar{1}$.

Crystal Packing of Ferric Wheels **5a–i of Space Group $R\bar{3}$ or $P\bar{3}$.** The ferric wheels $[\text{Fe}_6\text{X}_6(\text{L}^3)_6]$ (**5a–i**) have idealized S_6 molecular symmetry and crystallize in the space group $R\bar{3}$ (**5a–f, h, i**) or $P\bar{3}$ (**5g**) (Table 1). The crystal packing of the ferric wheels **5a–h** is pretty much the same. For example, all the disklike clusters of **5a** are arranged in parallel and are piled in cylindrical columns, with all the iron centers superimposed. Each column is surrounded by six parallel columns which are alternately dislocated by $1/3c$ and $2/3c$ against the central one (Figure 1).

The most significant difference between **5b** and **5c** is the arrangement of the ferric wheels to one another. For instance, in **5b** the mean intra- and intercolumnar midpoint distances amount to 12.6 and 21.9 Å, and for **5c** to 23.6 and 15.1 Å, respectively. It is clearly seen that, for **5b** and **5c**, the relative arrangement of the ferric wheels is reciprocally proportional. That is to say, large intercolumnar distances correspond with small intracolumnar distances and vice versa (Figure 2).

An additional interesting feature of some ferric wheels is their readiness to create various substructures, depending on the nature of their sidearms. For instance, van der Waals interactions cause the sidearms of **5e** and **5g**¹⁵ to interlock

(14) CCDC-231538 (**5a**), CCDC-230001 (**5b**), CCDC-231544 (**5c**), CCDC-231539 (**5d**), CCDC-231548 (**5e**), CCDC-231540 (**5f**), CCDC-231553 (**5g**), CCDC-211208 (**5h**), CCDC-230004 (**5i**), CCDC-231547 (**5j**), CCDC-231536 (**5k**), CCDC-231554 (**5l**), CCDC-231545 (**5m**), CCDC-231555 (**5n**), CCDC-231552 (**5o**), CCDC-231549 (**5p**), CCDC-230002 (**5q**), CCDC-230003 (**5r**), CCDC-231550 (**5s**), CCDC-231551 (**5t**), CCDC-231546 (**5u**), CCDC-231542 (**5v**), CCDC-231537 (**5w**), CCDC-231543 (**5x**), and CCDC-231541 (**5y**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/const/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, U.K.; fax (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

(15) Compound **5g** belongs to space group $P\bar{3}$ but is best discussed here.

Table 1. X-ray Crystallographic Data and Structure Refinements for Compounds **5a–y**

	5a^a	5b^b	5c^c	5d^a	5e^a
empirical formula	C ₆₆ H ₁₃₈ Cl ₆ Fe ₆ ·N ₆ O ₃₀ ·CHCl ₃	C ₄₈ H ₁₀₂ Cl ₆ Fe ₆ ·N ₆ O ₁₂ ·0.75CHCl ₃	C ₃₆ H ₇₈ Cl ₆ Fe ₆ ·N ₆ O ₁₂ ·2CHCl ₃	C ₁₀₂ H ₁₅₀ Fe ₆ ·N ₁₂ O ₃₀ S ₆	C ₇₂ H ₁₅₀ Cl ₆ Fe ₆ ·N ₆ O ₃₀ ·CHCl ₃
<i>M_r</i> [g mol ^{−1}]	2162.99	1592.68	1573.58	2551.80	2247.15
cryst size [mm ³]	0.35 × 0.35 × 0.30	0.45 × 0.40 × 0.28	0.35 × 0.30 × 0.30	0.35 × 0.30 × 0.20	0.40 × 0.30 × 0.20
cryst syst	rhombohedral	rhombohedral	rhombohedral	rhombohedral	rhombohedral
space group	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3	<i>R</i> 3
<i>T</i> [K]	173(2)	200(2)	275(2)	173(2)	173(2)
<i>a</i> [Å]	26.161(4)	21.919(2)	15.095(2)	25.0845(6)	26.731(4)
<i>b</i> [Å]					
<i>c</i> [Å]	12.283(3)	12.603(2)	23.647(3)	16.0454(7)	12.236(2)
α [deg]					
β [deg]					
γ [deg]					
<i>V</i> [Å ³]	7280(2)	5243.8(11)	4666.5(9)	8743.6(5)	7572(2)
<i>Z</i>	3	3	3	3	3
ρ _{calcd} [Mg m ^{−3}]	1.480	1.513	1.680	1.454	1.478
θ range [deg]	1.89–27.49	1.86–27.99	2.58–26.25	2.71–27.49	6.90–26.37
reflins collected	11425	3396	2352	9523	16083
unique reflns	3635	2741	2110	4168	3374
[<i>R</i> _{int}]	0.0437	0.0692	0.0608	0.0368	0.0270
reflins obsd [<i>I</i> > 2σ(<i>I</i>)]	3005	1924	1137	3316	3060
params	184	182	113	235	200
abs corr method	empirical (Scalepack)	ψ-scans	ψ-scans	empirical (Scalepack)	empirical (Scalepack)
final <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0435	0.0558	0.0716	0.0389	0.0348
<i>wR</i> 2 (all data)	0.1255	0.1461	0.2315	0.1138	0.0940
largest residuals [e Å ^{−3}]	0.624/−0.632	0.523/−0.581	1.395/−1.092	0.615/−0.442	0.716/−0.469
	5f^a	5g^a	5h^a	5i^a	5j^c
empirical formula	C ₇₈ H ₁₀₂ Fe ₆ N ₁₂ O ₁₈ ·S ₆ ·CHCl ₃ ·6CH ₂ Cl ₂	C ₉₀ H ₁₀₂ Cl ₆ Fe ₆ N ₆ ·O ₁₂ ·13CHCl ₃	C ₉₀ H ₁₀₂ Cl ₆ Fe ₆ N ₆ ·O ₁₂ ·H ₂ O	C ₁₂₀ H ₁₃₂ Cl ₆ Fe ₆ ·N ₁₂ O ₁₂ ·6CHCl ₃	C ₆₀ H ₁₂₆ Cl ₆ Fe ₆ ·N ₆ O ₂₄
<i>M_r</i> [g mol ^{−1}]	2652.10	3559.47	2020.68	3198.38	1859.44
cryst size [mm ³]	0.35 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.30	0.39 × 0.23 × 0.21	0.30 × 0.20 × 0.20
cryst syst	rhombohedral	hexagonal	rhombohedral	rhombohedral	monoclinic
space group	<i>R</i> 3	<i>P</i> 3	<i>R</i> 3	<i>R</i> 3	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> [K]	173(2)	173(2)	173(2)	100(2)	173(2)
<i>a</i> [Å]	29.0350(7)	32.4052(2)	30.060(3)	41.114(2)	17.101(3)
<i>b</i> [Å]					16.264(3)
<i>c</i> [Å]	11.8571(5)	11.8909(2)	12.127(2)	21.987(1)	15.114(3)
α [deg]					
β [deg]					96.74(3)
γ [deg]					
<i>V</i> [Å ³]	8656.7(5)	10813.7(3)	9490(2)	32187(3)	4174.4(14)
<i>Z</i>	3	3	3	9	2
ρ _{calcd} [Mg m ^{−3}]	1.526	1.639	1.105	1.485	1.479
θ range [deg]	1.90–27.46	1.26–27.49	3.71–25.02	3.32–27.51	1.20–27.49
reflins collected	8460	24880	4585	120889	9558
unique reflns	3932	15649	1937	16363	9558
[<i>R</i> _{int}]	0.0402	0.0348	0.0712	0.0657	0.0000 ^d
reflins obsd [<i>I</i> > 2σ(<i>I</i>)]	3121	9064	1426	11050	8276
params	221	836	190	775	468
abs corr method	empirical (Scalepack)	empirical (Scalepack)	empirical (Scalepack)	none	ψ-scans
final <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0817	0.0743	0.1001	0.0576	0.0406
<i>wR</i> 2 (all data)	0.2556	0.2232	0.2760	0.1849	0.1589
largest residuals [e Å ^{−3}]	1.641/−1.130	1.725/−0.861	0.851/−0.380	1.655/−2.632	0.868/−1.268
	5k^a	5l^a	5m^c	5n^a	5o^a
empirical formula	C ₉₀ H ₁₂₆ Fe ₆ N ₁₂ ·O ₂₄ S ₆ ·4CH ₂ Cl ₂	C ₆₆ H ₉₀ Cl ₆ Fe ₆ N ₆ ·O ₁₂ ·2H ₂ O·4CHCl ₃	C ₄₂ H ₇₈ Cl ₆ Fe ₆ N ₆ ·O ₁₂ ·2CHCl ₃	C ₉₆ H ₁₃₈ Fe ₆ N ₁₂ ·O ₁₂ S ₆ ·4CHCl ₃	C ₆₆ H ₁₁₄ Fe ₆ N ₁₂ ·O ₂₄ S ₆ ·8CHCl ₃
<i>M_r</i> [g mol ^{−1}]	2627.19	2220.74	1645.68	2657.12	2942.10
cryst size [mm ³]	0.35 × 0.30 × 0.30	0.20 × 0.20 × 0.20	0.60 × 0.30 × 0.20	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)	173(2)
<i>a</i> [Å]	17.30930(10)	16.833(3)	13.074(3)	13.2578(4)	13.5427(2)
<i>b</i> [Å]	20.8732(2)	16.866(3)	11.660(2)	19.2200(3)	21.8038(3)
<i>c</i> [Å]	16.27560(10)	16.068(3)	22.592(5)	24.8933(8)	20.6024(4)
α [deg]					
β [deg]	91.0410(10)	106.81(3)	105.51(3)	96.6350(11)	97.3160(10)
γ [deg]					
<i>V</i> [Å ³]	5879.41(8)	4367.2(15)	3318.6(11)	6300.7(3)	6034.00(17)
<i>Z</i>	2	2	2	2	2
ρ _{calcd} [Mg m ^{−3}]	1.484	1.689	1.647	1.401	1.619
θ range [deg]	1.96–27.47	2.40–27.51	2.38–24.98	2.70–25.04	1.99–27.49
reflins collected	24701	18049	6092	21194	25527
unique reflns	13455	9951	5822	11015	13732
[<i>R</i> _{int}]	0.0196	0.0255	0.0366	0.0442	0.0329
reflins obsd [<i>I</i> > 2σ(<i>I</i>)]	10554	7731	4249	8204	9807
params	695	514	403	668	658
abs corr method	empirical (Scalepack)	empirical (Scalepack)	ψ-scans	empirical (Scalepack)	empirical (Scalepack)
final <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0363	0.0712	0.0434	0.0781	0.0593
<i>wR</i> 2 (all data)	0.1039	0.2344	0.1193	0.2334	0.1804
largest residuals [e Å ^{−3}]	0.718/−0.669	2.009/−1.622	0.974/−0.591	1.057/−0.850	2.477/−1.407

Table 1 (Continued)

	5p ^c	5q ^b	5r ^b	5s ^a	5t ^a
empirical formula	C ₆₀ H ₁₁₄ Cl ₆ Fe ₆ -N ₆ O ₁₂	C ₆₀ H ₁₂₆ Cl ₆ Fe ₆ N ₆ -O ₁₂ ·2CHCl ₃	C ₇₂ H ₁₅₀ Cl ₆ Fe ₆ -N ₆ O ₁₂	C ₈₄ H ₁₇₄ Cl ₆ -Fe ₆ N ₆ O ₁₂	C ₉₀ H ₁₇₄ Fe ₆ -N ₁₂ O ₁₂ S ₆
<i>M_r</i> [g mol ⁻¹]	1659.37	1910.20	1839.78	2008.09	2143.87
cryst size [mm ³]	0.30 × 0.30 × 0.30	0.65 × 0.45 × 0.22	0.38 × 0.26 × 0.20	0.35 × 0.35 × 0.30	0.35 × 0.30 × 0.30
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	C2/c	P1	P1	P1	P1
<i>T</i> [K]	173(2)	200(2)	200(2)	173(2)	173(2)
<i>a</i> [Å]	21.1158(4)	11.306(2)	12.056(1)	13.0050(2)	14.254(3)
<i>b</i> [Å]	16.4674(4)	13.128(1)	13.106(1)	13.8403(2)	15.202(3)
<i>c</i> [Å]	22.4019(5)	15.502(1)	15.006(2)	16.4992(2)	15.362(3)
α [deg]		110.07(1)	76.53(1)	65.7690(10)	115.01(3)
β [deg]	97.2888(13)	97.16(1)	78.46(1)	69.8380(10)	92.71(3)
γ [deg]		91.21(1)	84.73(1)	80.8020(10)	111.09(3)
<i>V</i> [Å ³]	7726.7(3)	2139.3(4)	2256.7(4)	2541.57(6)	2735.0(10)
<i>Z</i>	4	1	1	1	1
ρ_{calcd} [Mg m ⁻³]	1.426	1.483	1.354	1.312	1.302
θ range [deg]	1.57–27.47	1.76–27.00	1.89–27.00	1.42–27.50	1.51–27.51
reflns collected	16854	10530	11249	21970	23824
unique reflns	8821	9118	9816	11633	12547
$[R_{\text{int}}]$	0.0388	0.0233	0.0449	0.0199	0.0199
reflns obsd [<i>I</i> > 2 σ (<i>I</i>)]	6065	7352	6063	9189	9807
params	410	635	460	514	568
abs corr method	ψ -scans	ψ -scans	ψ -scans	empirical (Scalepack)	empirical (Scalepack)
final <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0385	0.0386	0.0618	0.0361	0.0439
<i>wR</i> 2 (all data)	0.1014	0.1024	0.1481	0.1130	0.1423
largest residuals [e Å ⁻³]	0.613/–0.489	0.611/–0.474	1.374/–0.746	1.008/–0.730	1.345/–0.616

	5u ^c	5v ^a	5w ^a	5x ^a	5y ^a
empirical formula	C ₄₈ H ₁₀₂ Cl ₆ Fe ₆ -N ₆ O ₁₈ ·2CHCl ₃	C ₉₆ H ₁₅₀ Cl ₆ -Fe ₆ N ₆ O ₃₀	C ₁₀₈ H ₁₃₈ Cl ₆ -Fe ₆ N ₆ O ₂₄	C ₁₃₂ H ₁₅₀ Cl ₆ Fe ₆ N ₆ O ₂₄ ·2C ₅ H ₁₂ ·2CH ₂ Cl ₂	C ₁₀₂ H ₁₃₈ Cl ₆ Fe ₆ -N ₆ O ₂₄ ·Et ₂ O
<i>M_r</i> [g mol ⁻¹]	1833.89	2416.02	2452.04	3066.52	2454.10
cryst size [mm ³]	0.30 × 0.30 × 0.30	0.20 × 0.20 × 0.15	0.40 × 0.30 × 0.25	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.10
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	P1	P1	P1	P1	P1
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)	173(2)
<i>a</i> [Å]	12.420(3)	11.9911(2)	12.63210(10)	15.3262(5)	12.9941(2)
<i>b</i> [Å]	16.726(3)	15.0678(4)	15.0623(2)	15.7033(4)	14.8203(3)
<i>c</i> [Å]	18.384(4)	15.7072(4)	16.9855(2)	16.1823(5)	16.3250(3)
α [deg]	89.95(3)	87.4551(1)	110.0940(10)	79.255(2)	74.1320(10)
β [deg]	82.56(3)	80.3979(14)	100.3340(10)	76.0670(10)	77.8580(10)
γ [deg]	89.73(3)	75.6373(13)	105.6920(10)	76.438(2)	80.4040(10)
<i>V</i> [Å ³]	3786.8(13)	2710.74(11)	2786.29(5)	3639.61(19)	2936.37(9)
<i>Z</i>	2	1	1	1	1
ρ_{calcd} [Mg m ⁻³]	1.608	1.480	1.461	1.399	1.388
θ range [deg]	2.43–24.97	2.20–27.51	2.37–27.54	1.71–25.14	2.03–27.53
reflns collected	13984	23421	24235	24741	25519
unique reflns	13312	12433	12789	12930	13425
$[R_{\text{int}}]$	0.0682	0.0272	0.0232	0.0229	0.0485
reflns obsd [<i>I</i> > 2 σ (<i>I</i>)]	5197	9362	9858	10112	8283
params	857	949	676	832	677
abs corr method	ψ -scans	empirical (Scalepack)	empirical (Scalepack)	empirical (Scalepack)	empirical (Scalepack)
final <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0482	0.0332	0.0350	0.0800	0.0512
<i>wR</i> 2 (all data)	0.1803	0.0837	0.1023	0.2549	0.1456
largest residuals [e Å ⁻³]	0.890/–1.243	0.700/–0.369	0.405/–0.432	1.656/–1.079	0.696/–0.697

^a Nonius KappaCCD. ^b Siemens-P4. ^c Nonius MACH3. ^d The data have been collected on a four-circle diffractometer equipped with a scintillation counter. Only a set of symmetrically independent reflections has been collected.

and give rise to the formation of compartments occupied by chloroform. In contrast, the sidearms of **5d** give rise to a self-contained ball-shaped capsule, lacking further intermolecular interactions (Figure 3).

An especially interesting example of crystal packing leading to porous frameworks is caused by three-dimensional π - π stacking of the naphthyl groups of the sidearms of ferric wheels **5h** (Figure 4). This leads to two different kinds of voids. Of the voids formed outside and between discrete wheels, only the outside voids host water molecules. Self-assembly by hydrogen bonding, van der Waals interaction, and π - π stacking are widespread binding modes in supramolecular hybrid organic–inorganic 3D-networks.^{9,10}

Unlike **5a–h**, the ferric wheels of **5i** are not arranged in parallel but are rather three-dimensionally perpendicular, a well-known construction for 3D coordination polymers.¹⁶ In

5i, the interpenetrating sidearms create large loose-fitting voids (Figure 5).

Crystal Packing of Ferric Wheels 5j–l of Space Group P2₁/c. The ferric wheels [Fe₆X₆(L³)₆] (**5j–l**) have idealized S₂ (**5j,k**) and S₆ (**5l**) molecular symmetry and crystallize in the space group P2₁/c (Table 1). The crystal packing of the ferric wheels **5j–l** is almost identical and differs only by the included angle of the two groups of parallel wheels (Figure 6, top). For example, all the disklike clusters of **5j** are arranged in parallel in two orientations (Figure 6, center) and are piled in cylindrical columns, with all the iron centers superimposed. Whereas the interpenetrating sidearms of the ferric wheels **5j,k** are subject to van der Waals interactions,

(16) Saalfrank, R. W.; Maid, H.; Hampel, F.; Peters, K. *Eur. J. Inorg. Chem.* **1999**, 1859–1876.

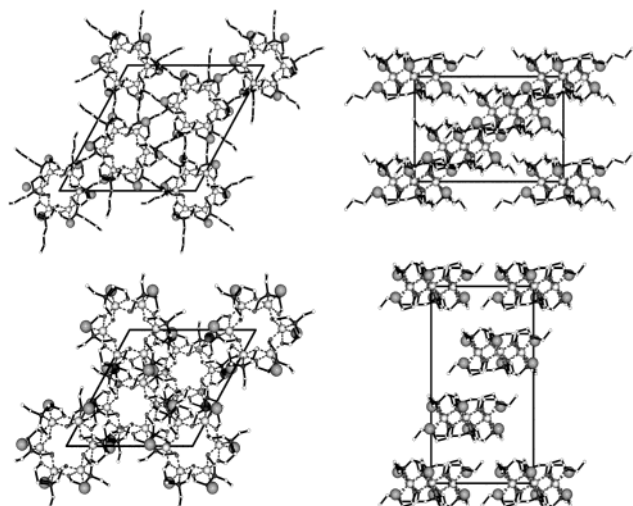


Figure 2. Presentation of the arrangement of the ferric wheels in **5b** (top) and **5c** (bottom). Left: view along the *c*-axis. Right: view along the *b*-axis.

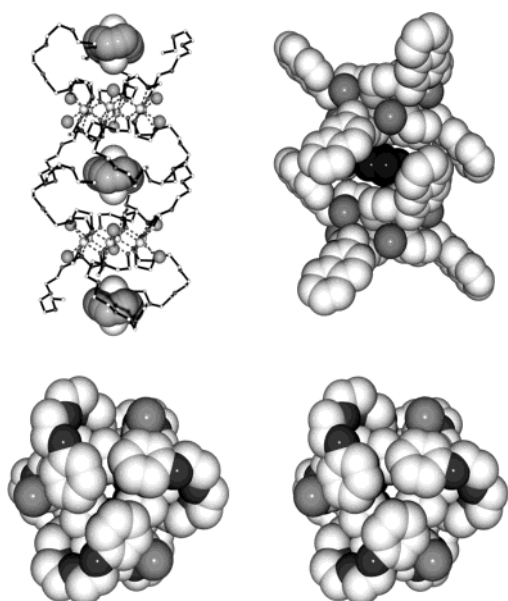


Figure 3. Top, left: presentation of the columnar crystal packing of **5e**, highlighting the compartments with encapsulated chloroform. Top, right: space-filling model, demonstrating the tight incarceration of chloroform by two interlocking entities of **5g**. Bottom: stereoview presentation of space-filling model of ball shaped **5d**.

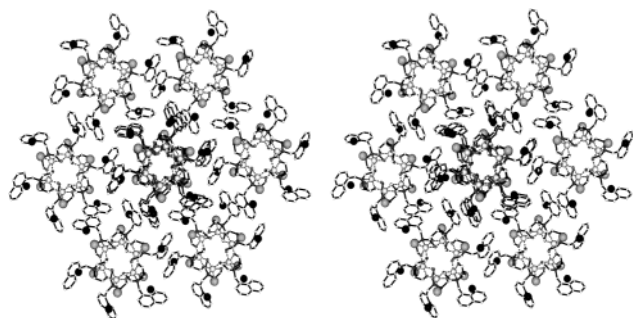


Figure 4. Stereoview of the crystal packing of **5h**, highlighting the π - π interactions together with encapsulated water (black spheres) in the outside voids.

the packing of the ferric wheels of **5l** is governed by π - π interactions (Figure 6, bottom).

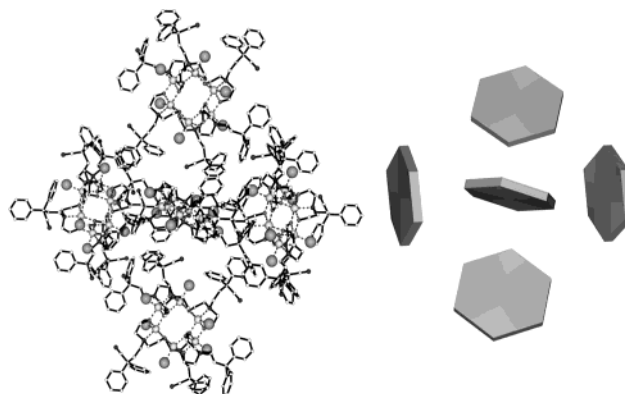


Figure 5. Left: crystal packing of **5i**. Right: graphical presentation, highlighting the three-dimensional perpendicular arrangement of the ferric wheels.

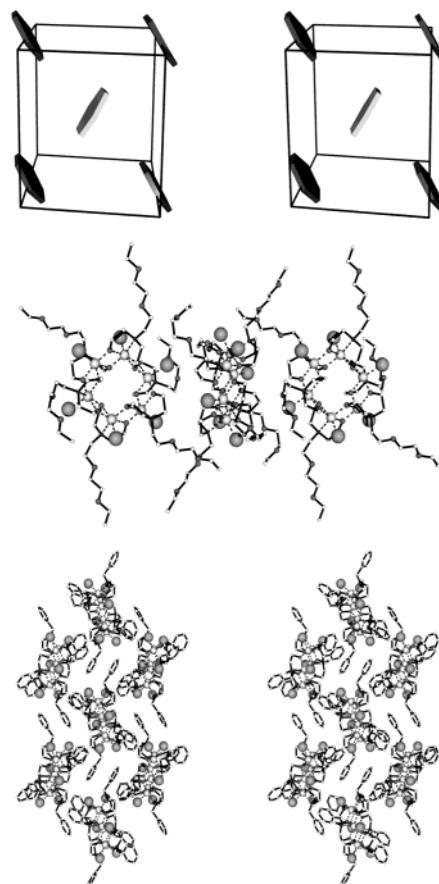


Figure 6. Top: schematic stereo presentation of the crystal packing of **5j-1**. Center: presentation of the two orientations of **5j**. Bottom: stereoview highlighting the one-dimensional π - π interactions between parallel complexes of **5l**.

Crystal Packing of Ferric Wheels 5m-o of Space Group $P2_1/n$ and 5p of Space Group $C2/c$. Whereas the unit cells of **5j-1** of space group $P2_1/c$ are most simply depicted with five wheels (Figure 6, top), the crystal packings of **5m-o** of space group $P2_1/n$ and **5p** of space group $C2/c$ are more complex. The unit cells of **5m-o** are basically represented by six wheels (Figure 7, top), and that for **5p** is represented by 15 wheels (Figure 7, bottom).

Crystal Packing of Ferric Wheels 5q-y of Space Group $P1$. The ferric wheels $[\text{Fe}_6\text{X}_6(\text{L}^3)_6]$ (**5q-y**) have idealized

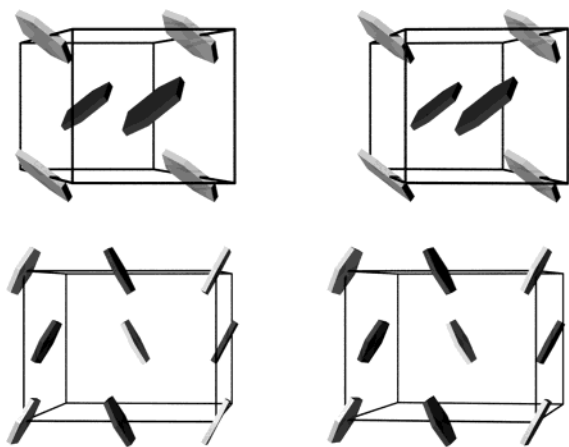


Figure 7. Schematic stereo presentation of the crystal packing of **5m-o** (top) and **5p** (bottom, for reasons of clarity only nine complexes are shown).

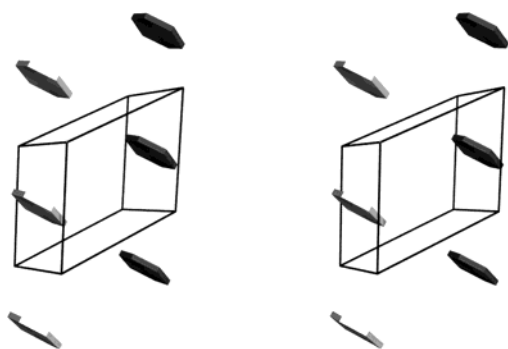


Figure 8. Schematic stereo presentation of the crystal packing of **5q-y**.

S_2 molecular symmetry and are packed in the crystal most simply, with all the ferric wheels piled in parallel (Figure 8).

Conclusion

Earlier, we described an efficient, simple route for the template-mediated self-assembly of iron(III) ions and triethanolamine to give six-membered iron coronates. Careful analysis of the construction plan of these systems was the basis for the rational design of six-membered iron coronands, starting from *N*-substituted diethanolamines and iron(III) chloride. Although the structures of the iron coronands are almost identical and have idealized S_6 or S_2 molecular symmetry, their variable sidearms give rise to a whole variety of different crystal packing modes. Most interestingly, the iron coronands readily frame compartments and three-dimensional networks with discrete channels and pores, suitable for the encapsulation of guest molecules. Aiming at the use of oligonuclear clusters as single-molecule magnets (SMMs), efforts toward crystal engineering are indispensable.

Experimental Section

General Techniques. All reactions were carried out under an atmosphere of dry nitrogen. All solvents used were purified and dried according to standard procedures. NMR spectra were recorded on JEOL EX 400 and JEOL GX 400 spectrometers. Solvent signals were employed as internal standards: CDCl_3 (^1H , 7.24 ppm; ^{13}C , 77.0 ppm); D_3CCOCD_3 (^1H , 2.04 ppm; ^{13}C , 29.30, 206.30 ppm).

General Method for H_2L^3 (4a-y**).** A suspension of the corresponding chloride, bromide, or toluenesulfonate (30 mmol), diethanolamine (1.1 equiv), and Na_2CO_3 (1.2 equivalents) in MeCN (125 mL) was heated at reflux for 48 h. The reaction mixture was then cooled, filtered to remove any residual salts, and concentrated under vacuum. The residue was taken up in CHCl_3 (100 mL) and washed with water (50 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum to give the product.¹⁷

4g-i,l-s. The corresponding halides were commercially available.

4a,e,j,u. The corresponding halides were prepared according to a literature procedure.¹⁸

4d,f,k,w,x. The corresponding toluenesulfonate compounds were prepared according to a literature procedure.¹⁹

4y. 3,5-Bis(allyloxy)benzyl bromide was prepared according to a literature procedure.²⁰

H_2L^3 (4a**).** Yield: 6.11 g (81%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3417, 2878, 1655, 1089 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 3.65–3.50 (m, 14H, 5 $\text{CH}_2\text{-O}$, 2 $\text{CH}_2\text{-OH}$), 3.34 (s, 3H, CH_3), 2.71 (t, 2H, J = 5.0 Hz, $\text{CH}_2\text{-N}$), 2.66 (t, 4H, J = 5.0 Hz, 2 N-CH_2) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): δ = 71.84, 70.38 (two superimposed peaks), 70.17, 69.55 (5 $\text{CH}_2\text{-O}$), 59.71 (2 $\text{CH}_2\text{-OH}$), 58.92 ($\text{CH}_3\text{-O}$), 57.27 (2 N-CH_2), 54.02 ($\text{CH}_2\text{-N}$) ppm. FAB-MS (3-NBA): m/z (%) = 252 (100) $[\text{M}]^+$, 220 (40) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{11}\text{H}_{25}\text{NO}_5$ (251.32): C 52.57, H 10.03, N 5.57. Found: C 49.73, H 10.17, N 4.54.

H_2L^3 (4b,c**).** Commercially available.

H_2L^3 (4d**).** Yield: 8.74 g (93%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3373, 2874, 1059, 757, 693 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.25–7.21 (m, 2H, 2 Ar-H), 6.92–6.88 (m, 3H, 3 Ar-H), 4.11 (t, 2H, J = 4.9 Hz, $\text{CH}_2\text{-O}$), 3.81 (t, 2H, J = 4.9 Hz, $\text{CH}_2\text{-O}$), 3.70–3.61 (m, 4H, 2 $\text{CH}_2\text{-O}$), 3.74–3.50 (m, 6H, $\text{CH}_2\text{-O}$, 2 $\text{CH}_2\text{-OH}$), 2.71 (t, 2H, J = 5.2 Hz, $\text{CH}_2\text{-N}$), 2.66 (t, 4H, J = 5.1 Hz, 2 N-CH_2) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): δ = 158.47 (Ar-C), 129.21, 120.64, 114.47 (5 Ar-CH), 70.62, 70.16, 69.66, 69.63, 67.18 (5 $\text{CH}_2\text{-O}$), 59.71 (2 $\text{CH}_2\text{-OH}$), 57.09 (2 N-CH_2), 53.82 ($\text{CH}_2\text{-N}$) ppm. FAB-MS (3-NBA): m/z (%) = 314 (100) $[\text{M}]^+$, 282 (45) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{16}\text{H}_{27}\text{NO}_5$ (313.39): C 61.32, H 8.68, N 4.47. Found: C 57.98, H 7.94, N 4.14.

H_2L^3 (4e**).** Yield: 3.34 g (42%) colorless oil. IR (neat): $\tilde{\nu}$ = 3385, 2950, 2873, 1452, 1112 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 3.61–3.42 (m, 16H, 2 $\text{CH}_2\text{-OH}$, 6 $\text{CH}_2\text{-O}$), 3.42 (br s, 2H, 2 OH), 2.76 (t, 2H, J = 5.1 Hz, $\text{CH}_2\text{-N}$), 2.72 (t, 4H, J = 5.1 Hz, 2 N-CH_2), 1.21 (t, 3H, J = 7.1 Hz, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): δ = 70.65, 70.49, 70.27, 69.81, 69.65, 66.63 (6 $\text{CH}_2\text{-O}$), 59.78 (2 $\text{CH}_2\text{-OH}$), 57.28 (2 N-CH_2), 54.04 ($\text{CH}_2\text{-N}$), 15.15 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 265 (5) $[\text{M}]^+$, 234 (100) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{12}\text{H}_{27}\text{NO}_2$ (265.35): C 54.32, H 10.26, N 5.28. Found: C 52.50, H 10.02, N 4.72.

H_2L^3 (4f**).** Yield: 6.42 g (95%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3359, 2949, 2879, 1037, 756, 693 cm^{-1} . ^1H NMR (400 MHz,

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CDCl₃): δ = 7.30–7.23 (m, 2H, 2 Ar–H), 6.95–6.87 (m, 3H, 3 Ar–H), 4.02 (t, 2H, J = 5.1 Hz, CH₂–O), 3.60 (t, 4H, J = 5.2 Hz, 2 CH₂–OH), 2.94 (t, 2H, J = 5.1 Hz, CH₂–N), 2.74 (t, 4H, J = 5.2 Hz, 2 N–CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 158.34 (Ar–C), 129.50, 121.08, 114.46 (5 Ar–CH), 66.22 (O–CH₂), 59.68 (2 N–CH₂), 56.87 (2 CH₂–OH), 53.48 (CH₂–N) ppm. FAB-MS (3-NBA): m/z (%) = 226 (100) [M]⁺, 194 (50) [M – CH₂OH]⁺. Anal. Calcd (%) for C₁₂H₁₉NO₃ (225.28): C 63.98, H 8.50, N 6.22. Found: C 60.96, H 8.68, N 5.81.

H₂L³ (4g). Yield: 5.08 g (69%) thick pale yellow oil. IR (neat): $\tilde{\nu}$ = 3355, 3054, 1690, 1406, 1037 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 7.79–7.69 (m, 4H, 4 Naph–H), 7.47–7.45 (m, 1H, 1 Naph–H), 7.44–7.42 (m, 1H, 1 Naph–H), 7.24 (br s, 1H, 1 Naph–H), 3.79 (s, 2H, CH₂–N), 3.58 (t, 4H, J = 5.4 Hz, 2 CH₂–OH), 3.57 (br s, 2H, 2 OH), 2.68 (t, 4H, J = 5.4 Hz, 2 N–CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 136.36, 133.27, 132.27, 129.09, 128.45, 127.89, 127.37, 127.09, 126.05, 125.68 (3 Naph–C, 7 Naph–CH), 59.61 (2 CH₂–OH), 59.43 (CH₂–N), 55.98 (2 N–CH₂) ppm. MS (EI, 70 eV): m/z (%) = 245 (10) [M]⁺, 214 (20) [M – CH₂OH]⁺, 141 (100) [M – N(CH₂CH₂OH)₂]⁺. Anal. Calcd (%) for C₁₅H₁₉NO₂ (245.33): C 73.44, H 7.81, N 5.71. Found: C 73.59, H 7.93, N 5.67.

H₂L³ (4h). Yield: 5.12 g (74%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3396, 2946, 2881, 1406, 1064 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 8.13–7.96 (m, 4H, 4 Naph–H), 7.81–7.79 (m, 1H, 1 Naph–H), 7.48–7.37 (m, 1H, 1 Naph–H), 7.18 (br s, 1H, 1 Naph–H), 4.09 (s, 2H, CH₂–N), 3.53 (t, 4H, J = 5.3 Hz, 2 CH₂–OH), 3.14 (br s, 2H, 2 OH), 2.65 (t, 4H, J = 5.3 Hz, 2 N–CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 134.44, 133.87, 133.27, 132.75, 132.21, 128.67, 127.64, 127.04, 125.16, 123.90 (3 Naph–C, 7 Naph–CH), 59.74 (2 CH₂–OH), 58.34 (CH₂–N), 56.12 (2 N–CH₂) ppm. MS (EI, 70 eV): m/z (%) = 245 (10) [M]⁺, 214 (20) [M – CH₂OH]⁺, 142 (100) [M – N(CH₂CH₂OH)₂]⁺. Anal. Calcd (%) for C₁₅H₁₉NO₂ (245.33): C 73.44, H 7.81, N 5.71. Found: C 73.51, H 7.79, N 5.68.

H₂L³ (4i). Yield: 7.10 g (66%) colorless oil that solidifies on standing. IR (neat): $\tilde{\nu}$ = 3377, 3060, 2953, 2250, 1598, 1448, 1033 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 7.41–7.26 (m, 10H, 10 Ar–H), 3.64 (t, 4H, J = 5.4 Hz, 2 CH₂–OH), 3.30 (t, 4H, J = 5.3 Hz, 2 N–CH₂), 3.22 (br s, 2H, 2 OH), 2.90 (t, J = 5.4 Hz, 2H, C_q–CH₂), 2.64 (t, 2H, J = 5.4 Hz, CH₂–N), 2.55 (t, 2H, J = 5.4 Hz, 2 N–CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 129.11, 128.92, 128.31, 128.28, 127.98, 127.76, 127.56, 126.95, 126.64, 126.54, 126.21, 126.04 (2 Ar–C, 10 Ar–CH), 119.16 (CN), 59.37 (2 CH₂–OH), 56.11 (2 N–CH₂), 53.10 (CH₂–N), 26.51 (C_q), 26.48 (C_q–CH₂) ppm. FAB-MS (3-NBA): m/z (%) = 325 (100) [M]⁺, 293 (20) [M – CH₂OH]⁺. Anal. Calcd (%) for C₂₀H₂₄N₂O₂ (324.43): C 74.04, H 7.46, N 8.64. Found: C 74.17, H 7.39, N 8.66.

H₂L³ (4j). Yield: 3.05 g (46%) colorless oil. IR (neat): $\tilde{\nu}$ = 3390, 2950, 2870, 1451, 1108 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 3.63 (t, 4H, J = 4.2 Hz, 2 CH₂–OH), 3.56 (m, 8H, 4 CH₂–O), 3.38 (br s, 2H, 2 OH), 2.76 (t, 2H, J = 5.1 Hz, CH₂–N), 2.72 (t, 4H, J = 4.6 Hz, 2 N–CH₂), 1.22 (t, 3H, J = 7.1 Hz, CH₃) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 70.23, 69.61, 69.50, 66.78 (4 CH₂–O), 59.74 (2 CH₂–OH), 57.28 (2 N–CH₂), 53.82 (CH₂–N), 14.98 (CH₃) ppm. MS (EI, 70 eV): m/z (%) = 221 (1) [M]⁺, 190 (60) [M – CH₂OH]⁺, 146 (19) [M – CH₂OH, – OC₂H₅]⁺, 118 (100) [M – CH₂OH, – C₂H₄OC₂H₅]⁺. Anal. Calcd (%) for C₁₀H₂₃NO₂ (221.30): C 54.28, H 10.48, N 6.33. Found: C 53.67, H 10.70, N 5.92.

H₂L³ (4k). Yield: 7.43 g (92%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3371, 2945, 2875, 1043, 756, 693 cm^{−1}. ¹H NMR (400 MHz,

CDCl₃): δ = 7.27–7.23 (m, 2H, Ar–H), 6.94–6.89 (m, 3H, Ar–H), 4.09 (t, 2H, J = 4.7 Hz, CH₂–O), 3.79 (t, 2H, J = 4.7 Hz, CH₂–O), 3.59 (t, 2H, J = 5.3 Hz, CH₂–O), 3.56 (t, 4H, J = 5.2 Hz, 2 CH₂–OH), 3.30 (br s, 2H, 2 OH), 2.75 (t, 2H, J = 5.3 Hz, CH₂–N), 2.68 (t, 4H, J = 5.2 Hz, 2 N–CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 158.47 (Ar–C), 129.41, 120.97, 114.52 (5 Ar–CH), 69.76, 69.43, 66.96 (3 CH₂–O), 59.68 (2 CH₂–OH), 56.96 (2 N–CH₂), 53.72 (CH₂–N) ppm. FAB-MS (3-NBA): m/z (%) = 270 (100) [M]⁺, 238 (50) [M – CH₂OH]⁺. Anal. Calcd (%) for C₁₄H₂₃NO₄ (269.34): C 62.43, H 8.61, N 5.20. Found: C 59.73, H 8.53, N 4.63.

H₂L³ (4l). Yield: 5.27 g (90%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3353, 2947, 2880, 2826, 1039, 734, 700 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 7.24–7.16 (m, 5H, 5 Ar–H), 3.61 (s, 2H, CH₂–N), 3.52 (t, 4H, J = 5.3 Hz, 2 CH₂–OH), 3.19 (br s, 2H, 2 OH), 2.61 (t, 4H, J = 5.3 Hz, 2 N–CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 139.07 (Ar–C), 129.39, 128.84, 127.90 (5 Ar–CH), 59.97 (2 CH₂–OH), 59.59 (CH₂–N), 56.14 (2 N–CH₂) ppm. FAB-MS (3-NBA): m/z (%) = 196 (100) [M]⁺, 164 (70) [M – CH₂–OH]⁺. Anal. Calcd (%) for C₁₁H₁₇NO₂ (195.26): C 67.66, H 8.78, N 7.17. Found: C 65.65, H 8.95, N 6.88.

H₂L³ (4m). Yield: 2.61 g (60%) yellow oil. IR (neat): $\tilde{\nu}$ = 3347, 3077, 2955, 2882, 2823, 1643, 1077, 921 cm^{−1}. ¹H NMR (400 MHz, CD₃COCD₃): δ = 5.87 (m, 1H, CH₂=CH), 5.14 (m, 2H, CH₂=CH), 3.62 (br s, 2H, 2 OH), 3.55 (t, 4H, J = 5.6 Hz, 2 CH₂–OH), 3.20 (d, 2H, J = 6.4 Hz, CH₂–N), 2.63 (t, 4H, J = 5.6 Hz, 2 N–CH₂). ¹³C NMR (100.5 MHz, CD₃COCD₃): δ = 137.04 (CH₂=CH), 117.26 (CH₂=CH), 60.27 (2 CH₂–OH), 58.59 (CH₂–N), 57.06 (2 N–CH₂) ppm. MS (EI, 70 eV): m/z (%) = 145 (4) [M]⁺, 114 (100) [M – CH₂OH]⁺. Anal. Calcd (%) for C₇H₁₅NO₂ (145.20): C 57.90, H 10.41, N 9.65. Found: C 54.41, H 9.11, N 9.83.

H₂L³ (4n). Yield: 7.16 g (95%) colorless oil. IR (neat): $\tilde{\nu}$ = 3356, 2961, 2875, 1364, 1038 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 7.32 (d, 2H, J = 8.3 Hz, 2 Ar–H), 7.21 (d, 2H, J = 8.8 Hz, 2 Ar–H), 3.65 (s, 2H, CH₂–N), 3.60 (t, 4H, J = 5.5 Hz, 2 CH₂–OH), 2.78 (br s, 2H, 2 OH), 2.69 (t, 4H, J = 5.5 Hz, 2 N–CH₂), 1.29 (s, 9H, 3 CH₃) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 150.15, 135.49 (2 Ar–C), 128.56, 125.32 (4 Ar–CH), 59.56 (2 CH₂–OH), 58.78 (CH₂–N), 55.64 (2 N–CH₂), 34.42 (tBu–C_q), 31.33 ppm (3 CH₃). FAB-MS (3-NBA): m/z (%) = 252 (75) [M]⁺, 220 (45) [M – CH₂OH]⁺, 147 (100) [M – N(CH₂CH₂OH)₂]⁺. Anal. Calcd (%) for C₁₅H₂₅NO₂ (251.37): C 71.67, H 10.03, N 5.57. Found: C 70.28, H 10.15, N 5.20.

H₂L³ (4o). Yield: 5.70 g (81%) thick pink oil. IR (neat): $\tilde{\nu}$ = 3422, 2964, 2797, 1610, 1045 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 4.62 (t, 1H, J = 5.4 Hz, CH–O), 3.98 (m, 2H, CH₂–CH–O), 3.46 (t, 4H, J = 5.4 Hz, 2 CH₂–O), 3.30 (t, 4H, J = 5.4 Hz, 2 CH₂–OH), 3.22 (br s, 2H, 2 OH), 2.61 (t, 2H, J = 5.4 Hz, CH₂–N), 2.58 (t, 4H, J = 5.4 Hz, 2 N–CH₂), 1.59 (m, 2H, CH₂–CH₂–O) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ = 101.35 (CH–O), 67.21 (2 CH₂–O), 60.48 (2 CH₂–OH), 55.84 (2 N–CH₂), 48.44 (CH₂–N), 32.32 (CH₂–CH–O), 25.44 (CH₂–CH₂–O) ppm. MS (EI, 70 eV): m/z (%) = 219 (5) [M]⁺, 188 (10) [M – CH₂OH]⁺, 130 (10) [M – NCH₂CH₂OH]⁺, 83 (100) [M – CH₂ – N(CH₂–CH₂OH)₂]⁺. Anal. Calcd (%) for C₁₀H₂₁NO₄ (219.29): C 54.77, H 9.65, N 6.39. Found: C 53.96, H 9.41, N 6.28.

H₂L³ (4p). Yield: 3.20 g (57%) yellow oil. IR (neat): $\tilde{\nu}$ = 3354, 3079, 2946, 2881, 2827, 1639, 1047, 910 cm^{−1}. ¹H NMR (400 MHz, CDCl₃): δ = 5.80 (m, 1H, CH₂=CH), 5.10 (m, 2H, CH₂=CH), 3.61 (t, 4H, J = 5.6 Hz, 2 CH₂–OH), 3.25 (br s, 2H, 2 OH), 2.65 (t, 4H, J = 5.6 Hz, 2 N–CH₂), 2.64 (t, 2H, J = 7.1 Hz, CH₂–N), 2.30 (m, 6H, 3 CH₂) ppm. ¹³C NMR (100.5 MHz, CDCl₃):

$\delta = 136.40$ ($\text{CH}_2=\text{CH}$), 116.12 ($\text{CH}_2=\text{CH}$), 69.42 ($2 \text{ CH}_2-\text{OH}$), 55.85 (CH_2-N), 53.65 ($2 \text{ N}-\text{CH}_2$), 32.12 , 31.68 , 31.44 (3 CH_2) ppm. MS (EI, 70 eV): m/z (%) = 187 (8) $[\text{M}]^+$, 156 (100) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{10}\text{H}_{21}\text{NO}_2$ (187.28): C 64.13, H 11.30, N 7.48. Found: C 63.74, H 11.28, N 7.32.

H_2L^3 (4g). Yield: 2.73 g (48%) colorless oil. IR (neat): $\tilde{\nu} = 3346$, 2929, 2858, 1466, 1047 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 3.61$ (t, 4H, $J = 5.4$ Hz, $2 \text{ CH}_2-\text{OH}$), 3.18 (br s, 2H, 2 OH), 2.65 (t, 4H, $J = 5.4$ Hz, $2 \text{ N}-\text{CH}_2$), 2.52 (t, 2H, $J = 7.6$ Hz, CH_2-N), 1.44 (m, 2H, CH_2-CH_3), 1.28 (m, 6H, 3 CH_2) 0.89 (t, 3H, $J = 7.1$ Hz, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 59.63$ ($2 \text{ CH}_2-\text{OH}$), 56.06 (CH_2-N), 54.80 ($2 \text{ N}-\text{CH}_2$), 31.71, 27.00, 26.96, 22.59 (4 CH_2), 13.99 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 189 (6) $[\text{M}]^+$, 158 (100) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{10}\text{H}_{23}\text{NO}_2$ (189.31): C 63.45, H 12.25, N 7.40. Found: C 60.77, H 11.99, N 6.91.

H_2L^3 (4r). Yield: 2.93 g (45%) colorless oil. IR (neat): $\tilde{\nu} = 3355$, 2925, 2855, 1465, 1043 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 3.61$ (t, 4H, $J = 5.4$ Hz, $2 \text{ CH}_2-\text{OH}$), 3.15 (br s, 2H, 2 OH), 2.65 (t, 4H, $J = 5.4$ Hz, $2 \text{ N}-\text{CH}_2$), 2.53 (t, 2H, $J = 7.6$ Hz, CH_2-N), 1.46 (m, 2H, CH_2-CH_3), 1.27 (m, 10H, 5 CH_2), 0.88 (t, 3H, $J = 6.6$ Hz, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 59.63$ ($2 \text{ CH}_2-\text{OH}$), 56.13 (CH_2-N), 54.86 ($2 \text{ N}-\text{CH}_2$), 31.86, 29.54, 29.31, 27.42, 26.97, 22.66 (6 CH_2), 14.10 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 217 (4) $[\text{M}]^+$, 186 (100) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{12}\text{H}_{27}\text{NO}_2$ (217.35): C 66.31, H 12.52, N 6.44. Found: C 65.95, H 12.74, N 6.41.

H_2L^3 (4s). Yield: 3.90 g (73%) yellow oil. IR (neat): $\tilde{\nu} = 3370$, 2980, 2881, 1466, 1068, 766 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 3.62$ (t, 4H, $J = 5.4$ Hz, $2 \text{ CH}_2-\text{OH}$), 3.21 (br s, 2H, 2 OH), 2.72 (t, 4H, $J = 5.4$ Hz, $2 \text{ N}-\text{CH}_2$), 1.64 (m, 18H, 9 CH_2), 0.96 (t, 3H, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 61.42$ ($2 \text{ CH}_2-\text{OH}$), 55.95 ($2 \text{ N}-\text{CH}_2$), 55.85 (CH_2-N), 33.24, 32.19, 31.89, 28.74, 28.15, 27.36, 26.93, 26.17, 22.66 (9 CH_2), 19.33 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 245 (10) $[\text{M}]^+$, 214 (100) $[\text{M} - \text{CH}_2-\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{14}\text{H}_{31}\text{NO}_2$ (245.41): C 68.52, H 12.73, N 5.71. Found: C 67.16, H 12.96, N 5.49.

H_2L^3 (4t). Same as 4s.

H_2L^3 (4u). Yield: 2.55 g (48%) colorless oil. IR (neat): $\tilde{\nu} = 3373$, 2949, 2869, 1447, 1114 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 3.57$ (br s, 2H, 2 OH), 3.52 (t, 4H, $J = 5.4$ Hz, $2 \text{ CH}_2-\text{OH}$), 3.47 (m, 4H, $2 \text{ CH}_2-\text{O}$), 2.75 (t, 2H, $J = 5.9$ Hz, CH_2-N), 2.69 (t, 4H, $J = 5.4$ Hz, $2 \text{ N}-\text{CH}_2$), 1.13 (t, 3H, $J = 7.0$ Hz, CH_3) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 69.88$, 66.65 ($2 \text{ CH}_2-\text{O}$), 60.48 ($2 \text{ CH}_2-\text{OH}$), 58.06 ($2 \text{ N}-\text{CH}_2$), 53.82 (CH_2-N), 15.68 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 177 (6) $[\text{M}]^+$, 146 (61) $[\text{M} - \text{CH}_2\text{OH}]^+$, 118 (100) $[\text{M} - \text{CH}_2\text{OH} - \text{CH}_2\text{OC}_2\text{H}_5]^+$. Anal. Calcd (%) for $\text{C}_8\text{H}_{19}\text{NO}_2$ (177.24): C 54.21, H 10.81, N 7.90. Found: C 53.27, H 10.96, N 7.96.

H_2L^3 (4v). Same as 4d.

H_2L^3 (4w). Yield: 8.62 g (90%) pale red oil. IR (neat): $\tilde{\nu} = 3371$, 2942, 2875, 1047, 757, 692 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 8.28-8.26$ (m, 1H, Naph-H), 7.78-7.76 (m, 1H, Naph-H), 7.47-7.32 (m, 4H, 4 Naph-H), 6.81-6.79 (m, 1H, Naph-H), 4.28 (t, 2H, $J = 4.8$ Hz, CH_2-O), 3.95 (t, 2H, $J = 4.8$ Hz, CH_2-O), 3.67 (t, 2H, $J = 5.2$ Hz, CH_2-O), 3.56 (t, 4H, $J = 5.2$ Hz, $2 \text{ CH}_2-\text{OH}$), 2.79 (t, 2H, $J = 5.2$ Hz, CH_2-N), 2.70 (t, 4H, $J = 5.2$ Hz, $2 \text{ N}-\text{CH}_2$) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 154.41$, 134.49, 127.39, 126.38, 125.75, 125.64, 125.20, 122.01, 120.58, 104.99 ($3 \text{ Naph}-\text{C}$, 7 Naph-CH), 70.10, 69.61, 67.67 ($3 \text{ CH}_2-\text{O}$), 59.78 ($2 \text{ CH}_2-\text{OH}$), 56.95 ($2 \text{ N}-\text{CH}_2$), 53.92 (CH_2-N) ppm. FAB-MS (3-NBA): m/z (%) = 320 (100) $[\text{M}]^+$, 288 (80)

$[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{18}\text{H}_{25}\text{NO}_4$ (319.40): C 67.69, H 7.89, N 4.39. Found: C 64.67, H 7.72, N 4.08.

H_2L^3 (4x). Yield: 9.20 g (83%) pale red oil. IR (neat): $\tilde{\nu} = 3386$, 2942, 2875, 1047, 757, 692 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 7.52-7.46$ (m, 3H, 3 Ar-H), 7.34-7.25 (m, 4H, 4 Ar-H), 6.95-6.89 (m, 2H, 2 Ar-H), 4.21 (t, 2H, $J = 4.7$ Hz, CH_2-O), 3.90 (t, 2H, $J = 4.7$ Hz, CH_2-O), 3.72 (t, 2H, $J = 5.2$ Hz, CH_2-O), 3.52 (t, 4H, $J = 5.2$ Hz, $2 \text{ CH}_2-\text{OH}$), 2.72 (t, 2H, $J = 5.2$ Hz, CH_2-N), 2.65 (t, 4H, $J = 5.2$ Hz, $2 \text{ N}-\text{CH}_2$) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 159.23$ (Ar-C), 133.42, 131.48, 129.74, 128.28, 128.10 ($5 \text{ Ar}-\text{CH}$), 123.66 (Ar-C), 121.01 (Ar-CH), 113.09 (Ar-C), 112.60 (Ar-CH), 93.35, 85.91 ($2 \text{ C}\equiv$), 70.43, 69.52, 68.85 ($3 \text{ CH}_2-\text{O}$), 59.77 ($2 \text{ CH}_2-\text{OH}$), 56.85 ($2 \text{ N}-\text{CH}_2$), 53.94 (CH_2-N) ppm. FAB-MS (3-NBA): m/z (%) = 370 (100) $[\text{M}]^+$, 338 (40) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{22}\text{H}_{27}\text{NO}_4$ (369.45): C 71.52, H 7.37, N 3.79. Found: C 69.40, H 7.30, N 3.32.

H_2L^3 (4y). Yield: 7.38 g (80%) pale yellow oil. IR (neat): $\tilde{\nu} = 3371$, 2946, 2874, 1053, 995 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 6.48-6.47$ (m, 2H, 2 Ar-H), 6.37-6.36 (m, 1H, 1 Ar-H), 6.05-5.96 (m, 2H, 2 $\text{CH}=\text{CH}_2$), 5.37 (dd, 2H, $J = 17.0$ Hz, 1.6 Hz; $2 \text{ CH}=\text{CH}_2$ cis), 5.25 (d, 2H, $J = 9.9$ Hz, $2 \text{ CH}=\text{CH}_2$ trans), 4.47 (d, 4H, $J = 5.5$ Hz, $2 \text{ O}-\text{CH}_2$), 3.59 (s, 2H, CH_2-N), 3.58 (t, 4H, $J = 5.2$ Hz, $2 \text{ CH}_2-\text{OH}$), 2.67 (t, 4H, $J = 5.2$ Hz, $2 \text{ N}-\text{CH}_2$) ppm. ^{13}C NMR (100.5 MHz, CDCl_3): $\delta = 159.71$ ($2 \text{ Ar}-\text{C}$), 141.27 (Ar-C), 133.13 ($2 \text{ CH}=\text{CH}_2$), 117.70 ($2 \text{ CH}=\text{CH}_2$), 107.62 ($2 \text{ Ar}-\text{CH}$), 100.42 (Ar-CH), 68.77 ($\text{O}-\text{CH}_2$), 59.59 ($2 \text{ CH}_2-\text{OH}$), 59.36 (CH_2-N), 55.87 ($2 \text{ N}-\text{CH}_2$) ppm. FAB-MS (3-NBA): m/z (%) = 308 (100) $[\text{M}]^+$, 276 (80) $[\text{M} - \text{CH}_2\text{OH}]^+$. Anal. Calcd (%) for $\text{C}_{17}\text{H}_{25}\text{NO}_4$ (307.38): C 66.43, H 8.20, N 4.56. Found: C 63.44, H 8.17, N 4.20.

General Method for $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5a-c,e,g-j,l,m,p-s,u-y).

To a suspension of calcium hydride (189 mg, 4.5 mmol) in anhydrous THF (75 mL) was added H_2L^3 (4a-y) (3.0 mmol). After the suspension was stirred for 1 h at 20 °C, a solution of iron(III) chloride (487 mg, 3.0 mmol) in anhydrous THF (25 mL) was added. The reaction mixture was stirred at 20 °C for 72 h, and then, the solvent was removed under vacuum. The precipitate was dissolved in CH_2Cl_2 (50 mL), and the remaining residue was filtered off. After evaporation of the solvent, a yellow powder was obtained.

General Method for $[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]$ (5d,f,k,n,o,t). In order to prepare the rhodanide complexes, 3.0 mmol of the corresponding chloride complexes $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$, vide supra, were dissolved in CHCl_3 (50 mL), and a solution of KSCN (1.46 g, 15 mmol) in anhydrous MeOH (50 mL) was added. The reaction mixture was refluxed for 1 h (in the case of 5n, the suspension was stirred at 20 °C for 24 h), and then, the solvent was removed under vacuum. The precipitate was dissolved in CH_2Cl_2 (50 mL), and the remaining residue was filtered off. After evaporation of the solvent, a red powder was obtained.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5a). Educt: 4a (754 mg). Yield: 296 mg (29%) yellow rhombic crystals from chloroform/*n*-pentane. Mp 99 °C.²¹ IR (KBr): $\tilde{\nu} = 2869$, 1460, 1089 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2043 (1) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 2007 (10) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1325 (20) $[\text{Fe}_4\text{Cl}_3(\text{L}^3)_4]^+$, 701 (80) $[\text{Fe}_3\text{Cl}(\text{L}^3)_2]^+$, 645 (100) $[\text{Fe}_2\text{Cl}(\text{L}^3)_2]^+$. Anal. Calcd (%) for $\text{C}_{66}\text{H}_{138}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{30}$ (2043.61): C 38.79, H 6.82, N 3.68. Found: C 37.38, H 7.24, N 3.68.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5b). Educt: 4b (484 mg). Yield: 188 mg (25%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu} = 2958$, 2929, 2865, 1457, 1089 cm^{-1} . FAB-

(21) The low melting points of 5a,k,v,x (99, 117, 118, 100 °C) are noteworthy.

MS (3-NBA): m/z (%) = 1502 (52) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1469 (100) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1399 (88) $[\text{Fe}_6\text{Cl}_3(\text{L}^3)_6]^+$. Anal. Calcd (%) for $\text{C}_{48}\text{H}_{102}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1503.17): C 38.35, H 6.84, N 5.59. Found: C 34.88, H 6.10, N 4.65.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5c). Educat: **4c** (400 mg). Yield: 167 mg (25%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2970, 2934, 2903, 2858, 1473, 1447, 1077 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1334 (11) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1299 (15) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 759 (100) $[\text{Fe}_4\text{Cl}_4(\text{L}^3)_3]^+$. Anal. Calcd (%) for $\text{C}_{36}\text{H}_{78}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1334.36): C 32.39, H 5.89, N 6.30. Found: C 29.47, H 5.36, N 5.30.

$[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]$ (5d). Educat: **4d** (940 mg). Yield: 434 mg (34%) brown rhombic crystals from dichloromethane/*n*-pentane. Mp > 165 °C (dec). IR (KBr): $\tilde{\nu}$ = 2915, 2876, 2050, 1249, 1080 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2492 (5) $[\text{Fe}_6(\text{SCN})_5(\text{L}^3)_6]^+$, 1642 (10) $[\text{Fe}_4(\text{SCN})_3(\text{L}^3)_4]^+$, 1159 (15) $[\text{Fe}_3(\text{SCN})(\text{L}^3)_3]^+$, 849 (50) $[\text{Fe}_5(\text{SCN})(\text{L}^3)_3]^+$, 792 (50) $[\text{Fe}_4(\text{SCN})(\text{L}^3)_3]^+$, 734 (100) $[\text{Fe}_2(\text{L}^3)_2]^+$. Anal. Calcd (%) for $\text{C}_{102}\text{H}_{150}\text{Fe}_6\text{N}_{12}\text{O}_{30}\text{S}_6$ (2551.80): C 48.00, H 5.93, N 6.59. Found: C 47.24, H 5.73, N 6.45.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5e). Educat: **4e** (796 mg). Yield: 223 mg (21%) light yellow crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2974, 2904, 2868, 1458, 1441, 1142, 1089 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2127 (15) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 2091 (100) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1863 (45) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_5]^+$. Anal. Calcd (%) for $\text{C}_{72}\text{H}_{150}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{30}$ (2127.80): C 40.64, H 7.11, N 3.95. Found: C 39.22, H 7.20, N 3.51.

$[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]$ (5f). Educat: **4f** (676 mg). Yield: 233 mg (23%) brown rhombic crystals from dichloromethane/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2922, 2871, 2040, 1240, 1081 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1045 (100) $[\text{Fe}_5\text{Cl}_3(\text{L}^3)_3]^+$. Anal. Calcd (%) for $\text{C}_{78}\text{H}_{102}\text{Fe}_6\text{N}_{12}\text{O}_{18}\text{S}_6$ (2023.18): C 46.31, H 5.08, N 8.31. Found: C 45.19, H 5.22, N 8.37.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5g). Educat: **4g** (736 mg). Yield: 412 g (41%) yellow hexagonal crystals from chloroform/diethyl ether. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3024, 2866, 2250, 1081, 756 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2007 (55) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1972 (90) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1303 (25) $[\text{Fe}_4\text{Cl}_3(\text{L}^3)_4]^+$. Anal. Calcd (%) for $\text{C}_{90}\text{H}_{102}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (2007.67): C 53.84, H 5.12, N 4.19. Found: C 53.63, H 5.19, N 4.26.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5h). Educat: **4h** (736 mg). Yield: 446 mg (39%) yellow crystals from chloroform/diethyl ether. Mp > 240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3021, 2863, 2256, 1083, 758 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2008 (25) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1971 (40) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1303 (100) $[\text{Fe}_4\text{Cl}_3(\text{L}^3)_4]^+$. Anal. Calcd (%) for $\text{C}_{90}\text{H}_{102}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (2007.67): C 53.84, H 5.12, N 4.19. Found: C 53.45, H 5.09, N 4.19.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5i). Educat: **4i** (973 mg). Yield: 760 mg (41%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 200 °C (dec). IR (KBr): $\tilde{\nu}$ = 3443, 2906, 2865, 1493, 1086, 754, 698 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2483 (15) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 2444 (20) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 2160 (100) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_5]^+$, 1619 (40) $[\text{Fe}_4\text{Cl}_3(\text{L}^3)_4]^+$. Anal. Calcd (%) for $\text{C}_{120}\text{H}_{132}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (2482.30): C 58.06, H 5.36, N 6.77. Found: C 58.33, H 5.28, N 6.89.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5j). Educat: **4j** (664 mg). Yield: 205 mg (22%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2974, 2905, 2867, 1458, 1440, 1143, 1088 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1863 (12) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1827 (100) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1792 (6) $[\text{Fe}_4\text{Cl}_4(\text{L}^3)_3]^+$. Anal. Calcd (%) for $\text{C}_{60}\text{H}_{138}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{24}$ (1863.49): C 38.67, H 6.49, N 5.24. Found: C 46.20, H 8.42, N 5.24.

$[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]$ (5k). Educat: **4k** (808 mg). Yield: 332 mg (29%) brown rhombic crystals from dichloromethane/*n*-pentane. Mp 117 °C.²¹ IR (KBr): $\tilde{\nu}$ = 2930, 2870, 2046, 1248, 1082 cm^{-1} ; FAB-

MS (3-NBA): m/z (%) = 1467 (20) $[\text{Fe}_4(\text{SCN})_3(\text{L}^3)_4]^+$, 1408 (35) $[\text{Fe}_4(\text{SCN})_2(\text{L}^3)_4]^+$, 1027 (100) $[\text{Fe}_4(\text{SCN})(\text{L}^3)_3]^+$; elemental analysis calcd (%) for $\text{C}_{90}\text{H}_{126}\text{Fe}_6\text{N}_{12}\text{O}_{24}\text{S}_6$ (2287.50): C 47.25, H 5.56, N 7.35; found: C 47.23, H 5.74, N 6.91.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5l). Educat: **4l** (586 mg). Yield: 324 mg (38%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3062, 3030, 2909, 2865, 1496 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1707 (10) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1671 (25) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1513 (15) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_5]^+$, 1229 (15) $[\text{Fe}_5\text{Cl}_5(\text{L}^3)_4]^+$, 1101 (100) $[\text{Fe}_4\text{Cl}_3(\text{L}^3)_4]^+$, 1066 (40) $[\text{Fe}_4\text{Cl}_2(\text{L}^3)_4]^+$, 945 (70) $[\text{Fe}_4\text{Cl}_4(\text{L}^3)_3]^+$, 873 (35) $[\text{Fe}_4\text{Cl}_2(\text{L}^3)_3]^+$, 838 (25) $[\text{Fe}_4\text{Cl}(\text{L}^3)_3]^+$, 817 (95) $[\text{Fe}_3\text{Cl}_2(\text{L}^3)_3]^+$, 782 (100) $[\text{Fe}_3\text{Cl}(\text{L}^3)_3]^+$, 749 (75) $[\text{Fe}_3(\text{L}^3)_3]^+$. Anal. Calcd (%) for $\text{C}_{66}\text{H}_{90}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1707.24): C 46.43, H 5.31, N 4.92. Found: C 46.11, H 5.25, N 4.70.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5m). Educat: **4m** (436 mg). Yield: 197 mg (28%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3074, 3000, 2907, 2865, 1638, 1085, 929 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1406 (100) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$. Anal. Calcd (%) for $\text{C}_{42}\text{H}_{78}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1406.92): C 35.86, H 5.59, N 5.97. Found: C 32.45, H 4.93, N 4.81.

$[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]$ (5n). Educat: **4n** (754 mg). Yield: 606 mg (55%) red rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2963, 2928, 2869, 2032, 1460, 1264, 1081 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2179 (1) $[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]^+$, 2121 (4) $[\text{Fe}_6(\text{SCN})_5(\text{L}^3)_6]^+$, 1336 (35) $[\text{Fe}_4(\text{SCN})_2(\text{L}^3)_4]^+$, 1087 (30) $[\text{Fe}_4(\text{SCN})_2(\text{L}^3)_3]^+$, 973 (52) $[\text{Fe}_3(\text{SCN})(\text{L}^3)_3]^+$, 724 (100) $[\text{Fe}_3(\text{SCN})(\text{L}^3)_2]^+$. Anal. Calcd (%) for $\text{C}_{96}\text{H}_{138}\text{Fe}_6\text{N}_{12}\text{O}_{24}\text{S}_6$ (2179.73): C 52.90, H 6.38, N 7.71. Found: C 52.59, H 6.21, N 7.56.

$[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]$ (5o). Educat: **4o** (658 mg). Yield: 210 mg (35%) pink crystals from chloroform/*n*-pentane. Mp > 240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3490, 2864, 2250, 2190, 1250, 1088 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1987 (10) $[\text{Fe}_6(\text{SCN})_6(\text{L}^3)_6]^+$, 1928 (100) $[\text{Fe}_6(\text{SCN})_5(\text{L}^3)_6]^+$, 1266 (100) $[\text{Fe}_4(\text{SCN})_3(\text{L}^3)_4]^+$. Anal. Calcd (%) for $\text{C}_{66}\text{H}_{114}\text{Fe}_6\text{N}_{12}\text{O}_{24}\text{S}_6$ (1987.22): C 39.89, H 5.78, N 8.46. Found: C 39.58, H 5.82, N 7.58.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5p). Educat: **4p** (562 mg). Yield: 66 mg (8%) light green rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3098, 3072, 2909, 2870, 1638, 1081, 925 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1659 (100) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$. Anal. calcd (%) for $\text{C}_{60}\text{H}_{114}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1659.40): C 43.43, H 6.92, N 5.06. Found: C 42.34, H 7.05, N 4.87.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5q). Educat: **4q** (568 mg). Yield: 176 mg (21%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2956, 2927, 2859, 1458, 1089 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1671 (29) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1636 (94) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1483 (100) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_5]^+$. Anal. Calcd (%) for $\text{C}_{60}\text{H}_{126}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1671.50): C 43.12, H 7.60, N 5.03. Found: C 43.46, H 7.66, N 5.06.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5r). Educat: **4r** (652 mg). Yield: 166 mg (18%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3005, 2924, 2855, 1468, 1089 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 1837 (64) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 1802 (100) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$. Anal. Calcd (%) for $\text{C}_{72}\text{H}_{150}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (1839.82): C 47.00, H 8.22, N 4.57. Found: C 45.71, H 8.12, N 4.37.

$[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]$ (5s). Educat: **4s** (736 mg). Yield: 440 mg (36%) yellow crystals from dichloromethane/*n*-pentane. Mp > 240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3354, 2926, 2854, 1469, 1082 cm^{-1} . FAB-MS (3-NBA): m/z (%) = 2091 (50) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_6]^+$, 2055 (85) $[\text{Fe}_6\text{Cl}_5(\text{L}^3)_6]^+$, 1833 (80) $[\text{Fe}_6\text{Cl}_6(\text{L}^3)_5]^+$, 1485 (100) $[\text{Fe}_3\text{Cl}_3(\text{L}^3)_4]^+$. Anal. Calcd (%) for $\text{C}_{84}\text{H}_{174}\text{Cl}_6\text{Fe}_6\text{N}_6\text{O}_{12}$ (2008.18): C 50.24, H 8.73, N 4.19. Found: C 51.59, H 8.88, N 4.16.

[Fe₆(SCN)₆(L³)₆] (5t). Educt: **4t** (736 mg). Yield: 160 mg (30%) pink crystals from dichloromethane/*n*-pentane. Mp > 240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3440, 2925, 2855, 2247, 1084, 609 cm⁻¹. FAB-MS (3-NBA): *m/z* (%) = 2141 (10) [Fe₆(SCN)₆(L³)₆]⁺, 2085 (55) [Fe₆(SCN)₅(L³)₆]⁺, 1427 (80) [Fe₄(SCN)₄(L³)₄]⁺, 1370 (65) [Fe₄(SCN)₃(L³)₄]⁺, 1312 (70) [Fe₄(SCN)₂(L³)₄]⁺. Anal. Calcd (%) for C₉₀H₁₇₄Fe₆N₁₂O₁₂S₆ (2143.60): C 50.43, H 8.18, N 7.84, S 8.96. Found: C 50.68, H 8.19, N 7.93, S 9.04.

[Fe₆Cl₆(L³)₆] (5u). Educt: **4u** (532 mg). Yield: 144 mg (18%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2971, 2928, 2904, 2865, 1485, 1442, 1104, 1087 cm⁻¹. FAB-MS (3-NBA): *m/z* (%) = 1599 (26) [Fe₆Cl₆(L³)₆]⁺, 1563 (100) [Fe₆Cl₅(L³)₆]⁺, 1422 (24) [Fe₆Cl₆(L³)₅]⁺. Anal. Calcd (%) for C₄₈H₁₀₂Cl₆Fe₆N₆O₁₂ (1599.55): C 36.04, H 7.18, N 5.25. Found: C 32.60, H 5.86, N 4.42.

[Fe₆Cl₆(L³)₆] (5v). Educt: **4v** (940 mg). Yield: 519 mg (43%) yellow rhombic crystals from chloroform/diethyl ether. Mp 118 °C.²¹ IR (KBr): $\tilde{\nu}$ = 2910, 2870, 1598, 1493, 1248, 1087 cm⁻¹. FAB-MS (3-NBA): *m/z* (%) = 2416 (1) [Fe₆Cl₆(L³)₆]⁺, 2379 (5) [Fe₆Cl₅(L³)₆]⁺, 1575 (10) [Fe₄Cl₃(L³)₄]⁺, 825 (45) [Fe₃Cl(L³)₂]⁺, 769 (100) [Fe₂Cl(L³)₂]⁺. Anal. Calcd (%) for C₉₆H₁₅₀Cl₆Fe₆N₆O₃₀ (2416.02): C 47.72, H 6.62, N 3.48. Found: C 47.34, H 6.49, N 3.48.

[Fe₆Cl₆(L³)₆] (5w). Educt: **4w** (958 mg). Yield: 1.02 g (80%) yellow rhombic crystals from chloroform/*n*-pentane. Mp > 195 °C (dec). IR (KBr): $\tilde{\nu}$ = 2932, 2863, 1102, 1088 cm⁻¹. FAB-MS (3-NBA): *m/z* (%) = 1266 (100) [Fe₃Cl₃(L³)₃]⁺. Anal. Calcd (%) for C₁₀₈H₁₃₈Cl₆Fe₆N₆O₂₄ (2452.04): C 52.90, H 5.67, N 3.43. Found: C 51.72, H 5.20, N 3.18.

[Fe₆Cl₆(L³)₆] (5x). Educt: **4x** (1.11 g). Yield: 317 mg (23%) yellow rhombic crystals from dichloromethane/diethyl ether. Mp 100 °C.²¹ IR (KBr): $\tilde{\nu}$ = 2914, 2867, 1088 cm⁻¹. FAB-MS (3-NBA): *m/z* (%) = 2717 (2) [Fe₆Cl₅(L³)₆]⁺, 1800 (5) [Fe₄Cl₃(L³)₄]⁺, 1467 (5) [Fe₄Cl₄(L³)₃]⁺, 1339 (5) [Fe₃Cl₂(L³)₃]⁺, 972 (15) [Fe₃Cl(L³)₂]⁺, 937 (40) [Fe₃(L³)₂]⁺, 881 (100) [Fe₂(L³)₂]⁺. Anal. Calcd (%) for C₁₃₂H₁₅₀Cl₆Fe₆N₆O₂₄ (2752.42): C 57.60, H 5.49, N 3.05. Found: C 57.21, H 5.51, N 3.05.

[Fe₆Cl₆(L³)₆] (5y). Educt: **4y** (922 mg). Yield 619 mg (52%) yellow rhombic crystals from dichloromethane/*n*-pentane. Mp > 255 °C (dec). IR (KBr): $\tilde{\nu}$ = 2910, 2865, 1596, 1167, 1086 cm⁻¹. FAB-MS (3-NBA): *m/z* (%) = 2380 (3) [Fe₆Cl₆(L³)₆]⁺, 2343 (3) [Fe₆Cl₅(L³)₆]⁺, 2073 (3) [Fe₆Cl₆(L³)₅]⁺, 1551 (35) [Fe₄Cl₃(L³)₄]⁺, 1281 (30) [Fe₄Cl₄(L³)₃]⁺, 1154 (55) [Fe₃Cl₂(L³)₃]⁺, 1118 (55) [Fe₃Cl(L³)₃]⁺, 848 (60) [Fe₃Cl₂(L³)₃]⁺, 813 (90) [Fe₃Cl(L³)₃]⁺, 757 (100) [Fe₂Cl(L³)₂]⁺, 722 (60) [Fe₂(L³)₂]⁺. Anal. Calcd (%) for C₁₀₂H₁₃₈Cl₆Fe₆N₆O₂₄ (2380.00): C 51.47, H 5.84, N 3.53. Found: C 49.75, H 5.67, N 3.33.

Single-Crystal X-ray Structure Analyses. Final crystallographic data and R1 and wR2 values are listed in Table 1. X-ray data for all complexes were collected at low temperatures with a Nonius KappaCCD area detector, a Siemens-P4 diffractometer, or a Nonius MACH3 diffractometer using graphite monochromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-86 or SHELXS-97, and the structure refinements were carried out using full-matrix least-squares (SHELXL-93, SHELXL-97, or SHELXTL NT 5.10^{13,14}). All non-hydrogen atoms were refined anisotropically.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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