140. Trinuclear Double Helicates of Iron(II) and Nickel(II): Self-Assembly and Resolution into Helical Enantiomers

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Dedicated to *Vladimir Prelog* on the occasion of his 90th birthday

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The synthesis of the linear tris[terpyridine] **1** with three tridentate binding sites is described. The reaction with metal ions of octahedral coordination geometry, such as Fe^{II} or Ni^{II}, leads to the self-assembly of trinuclear complexes $[M_3(\mathbf{1})_2]^{6+}$, which display properties in agreement with a double helical structure. The trinuclear iron(II) helicate has been resolved into its enantiomers.

1. Introduction. – Helical inorganic architectures termed helicates have been shown to form by the spontaneous assembly of linear segmental ligands with transition-metal ions. The type of structure generated is determined by the nature and arrangement of the binding subunits in the ligand, and the coordination geometry of the metal ions which determine the steric program and the reading algorithm of the self-assembly process, respectively. Thus, homostrand double-helical complexes should be generated from bidentate or tridentate binding units with metal ions of tetrahedral or octahedral coordination, respectively, as schematically illustrated in *Fig. 1* [1–9]. Furthermore, pentacoor-

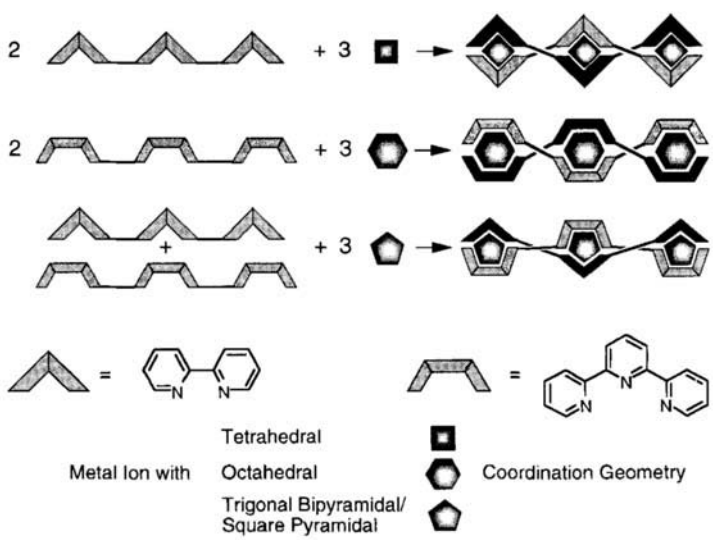


Fig. 1. *Modes of self-assembly of double helicates from ligands containing bidentate or tridentate binding sites and metal ions of various coordination geometry*

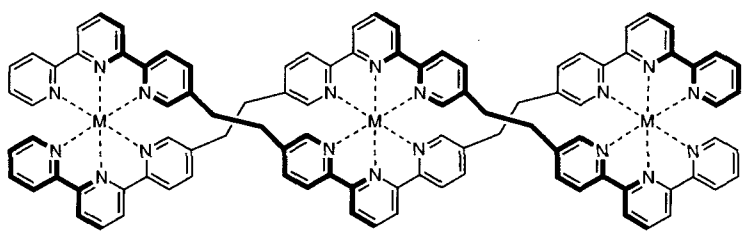
dinated metal ions should induce the self-assembly of a heterostrand double helicate containing one bidentate and one tridentate ligand strand (*Fig. 1*) [10].

On the other hand, triple-helical complexes result from the combination of bidentate sites with octahedral metal ions [4] [11–13] or tridentate sites with lanthanides [14].

Double-helical complexes have been obtained in particular by self-assembly of oligo(2,2′-bipyridine) ligands with Cu^{I} or Ag^{I} ions [1] [2] [15] and of a bis[2,2′:6′,2″-terpyridine] ligand with Fe^{II} and Ru^{II} [6]. Both types of ligand strands, bipyridine and terpyridine, could be combined in a heteroduplex helical architecture through pentacoordinated Cu^{II} ions [10].

One may consider these self-assembly processes to result from the reading of the steric information of the binding subunits by a specific metal ion following a given coordination algorithm [16], such as the formation of the DNA double helix results from the recognition-based interaction of the polynucleotide strands through complementary H-bonding patterns.

We now report the self-assembly of the trinuclear double helicates $[M_3(\mathbf{1})_2]^{6+}$ from a linear strand of three terpyridine units linked by C_2H_4 bridges, and Fe^{II} or Ni^{II} (*Fig. 2*), and the resolution of the $[Fe_3(\mathbf{1})_2]^{6+}$ species into its double helical enantiomers. At present, only the separation of a dinuclear triple helicate into its optically active components [17] and the spontaneous resolution of a trinuclear triple helical complex [11] have been reported.



$[Fe_3(\mathbf{1})_2]^{6+}$ M = Fe^{II}

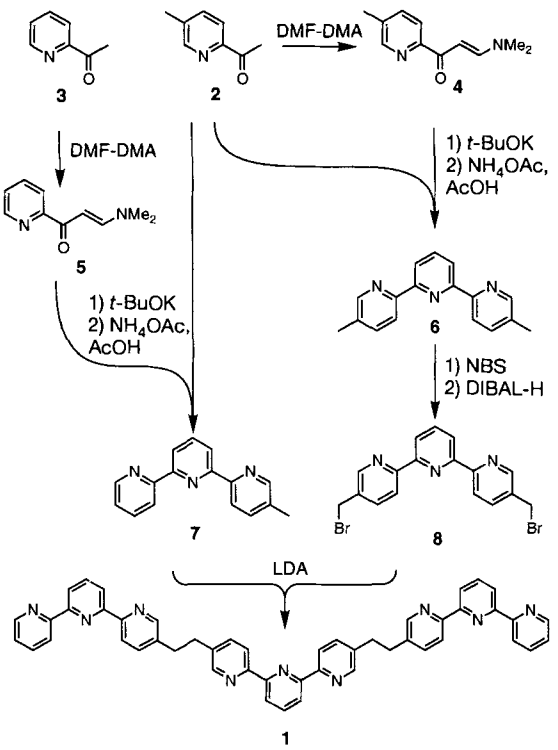
$[Ni_3(\mathbf{1})_2]^{6+}$ M = Ni^{II}

Fig. 2. *Trinuclear double helicates based on two linear tris[terpyridine] ligands* **1** *and three octahedrally coordinated metal ions*

2. Results and Discussion. – 2.1. *Synthesis of the Linear Ligand* **1**. The synthesis of the ligand **1** is based on the preparation of two differently substituted terpyridines **7** and **8**, and their final coupling to the tris[terpyridine] **1** (*Scheme*). This approach allows the modification of the nature of the spacer for further studies of its influence. Both terpyridines were prepared by a modified procedure reported for 2,2′:6′,2″-terpyridine itself [18]. The starting material, 2-acetyl-5-methylpyridine (**2**), was obtained by literature methods in two steps from 2-amino-5-methylpyridine [19–21]. The condensation of **2** or **3** with *N*,*N*-dimethylformamide dimethyl acetal (DMF-DMA) to give the ene-amines **4** and **5** required longer reaction times than reported and the presence of an acid catalyst. The reaction of **4** or **5** with **2** and NH_4OAc yielded the 5,5″-dimethyl-2,2′:6′,2″-terpyridine (**6**) [22] or 5-methyl-2,2′:6′,2″-terpyridine (**7**), respectively, in usual yields (35–40%) for this type of reaction. Radical bromination of **6** with an excess of *N*-bromosuccinimide (NBS)

gave **8** together with polybrominated products. Selective reduction of $CHBr_2$ groups to CH_2Br with DIBAL-H, as reported in the functionalization of related *N*-heteroaromatics [23], increased the yield and facilitated the purification of **8**. The final coupling of **7** with **8** in the presence of LDA gave the tris[terpyridine] ligand **1** as a solid, slightly soluble in polar organic solvents.

Scheme



2.2. *Assembly and Structure of the Double Helicates* $[M_3(\mathbf{1})_2]^{6+}$. Mixing 2 equiv. of tris[terpyridine] **1** with 3 equiv. of $Fe^{II}Cl_2$ in ethyleneglycol and heating to 170° afforded a purple solution. After 12 h, aqueous NH_4PF_6 was added to precipitate the complex. TLC Analysis showed only one major compound. Mass-spectroscopic analysis (ES and FAB) indicated the stoichiometry $[Fe_3(\mathbf{1})_2]$ $(PF_6)_6$. The ES-MS spectrum showed the successive loss of anions of the complex $[Fe_3(\mathbf{1})_2]$ $(PF_6)_4^{2+}$ down to $[Fe_3(\mathbf{1})_2]^{6+}$. No other compounds were detected. The ^{1}H-NMR spectrum displayed the typical shifts for $[Fe(terpy)_2]$ complexes, and 2D-COSY measurements allowed the identification of all signals (see *Exper. Part*). The spectra showed further that the $[Fe_3(\mathbf{1})_2]^{6+}$ species is symmetric around the central pyridine.

The CH_2CH_2 bridges between the terpyridine subunits in the ligand **1** are too short for the complexation of the same metal cation by two adjacent terpyridines of one strand. Binding of the two terminal terpyridines to the same metal ion would prevent the central subunit from binding. Ligand **1** should, therefore, be complexed by three cations, one at each site.

From these results, $[Fe_3(\mathbf{1})_2]^{6+}$ stoichiometry, two-fold symmetry, and geometric restrictions, two possible structures can be considered: the double helicate **A** and the side-by-side structure **B** (*Fig. 3*). They are expected to have different NMR spectra, so that the presence of only one set of signals excludes a mixture of the two isomers.

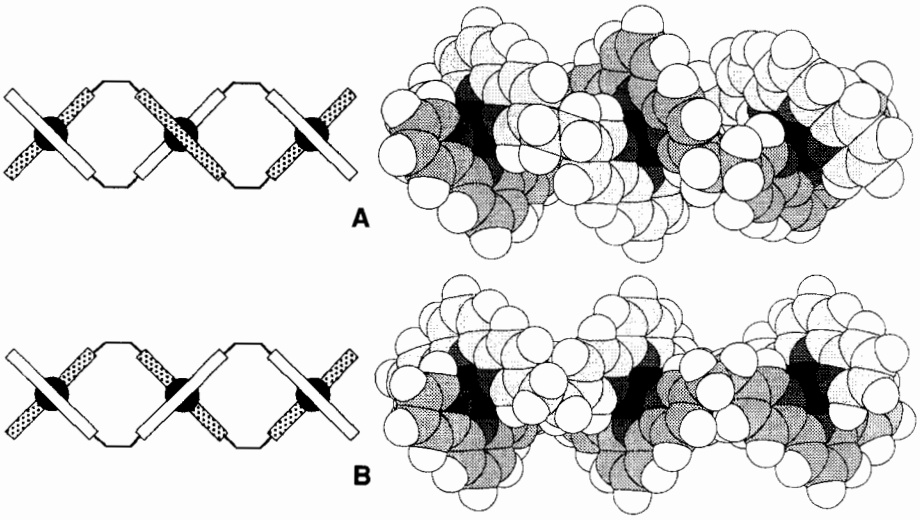


Fig. 3. *Schematic* (left) *and CPK* (right) *representations of the two possible diastereoisomers of the complexes* $[M_3(\mathbf{1})_2]^{6+}$. Top: *(*PPP*)-enantiomer of the homochiral double helicate;* Bottom: *(*PMP*)-enantiomer of the heterochiral 'side-by-side' structure.* The CPK representations are based on the crystal structure of $[Fe(terpy)_2](ClO_4)_2$ [24].

In the structure **B**, the protons H–C(4) on two adjacent terpyridines are in very close proximity. This steric hindrance should favor helical structure **A**. Further indication in favor of **A** is the similarity of the relaxation times of protons H–C(3) and H–C(4) on all terpyridines. This points to a similar chemical environment for these protons as it is the case in **A**, but not in **B**. Taking also into account the reported dinuclear double helicate formed with a bis[terpyridine] [6], the double-helicate structure **A** may be assigned to the complex $[Fe_3(\mathbf{1})_2]^{6+}$ [1]).

In an analogous way, the corresponding trinuclear Ni^{II} complex was formed from 2 equiv. of tris[terpyridine] **1** and 3 equiv. of $Ni^{II}Cl_2$, and isolated as the perchlorate salt. FAB-MS showed again the formation of the complex $[Ni_3(\mathbf{1})_2]$ $(ClO_4)_6$ as the only product. Absorption spectroscopy and microanalytical data were in agreement with this formulation. In view of the similar coordination properties of Ni^{II} and Fe^{II}, the double-helicate structure **A** may also be assigned to the complex $[Ni_3(\mathbf{1})_2]^{6+}$.

2.3. *Chromatographic Resolution of* $[Fe_3(\mathbf{1})_2]^{6+}$ *into Double-Helical Enantiomers.* A closer inspection of the chirality of the structures **A** and **B** in *Fig. 3* reveals the diastereoisomeric relationship between the two. The three metal centers in $[Fe_3(\mathbf{1})_2]^{6+}$ are chiral and exist, therefore, each as two enantiomers. Whereas the terminal terpyridine subunits are asymmetric and, therefore, give rise to chiral metal centers in the complex, the central terpyridine is symmetric. The chirality of the central metal ion in the trinuclear

[1]) **Note added in proof.** – The double-helicate structure **A** was confirmed recently by crystal structure determination (*B. Hasenknopf, J.-M. Lehn, G. Baum, D. Fenske*, unpublished results).

complex results solely from the geometric arrangement of the ligands. The three metal ions define an axis, with the terpyridine subunits wrapping around each metal center clockwise (plus, *P*) or counterclockwise (minus, *M*) [25]. By this definition, the structure **A** is identified as homochiral (*PPP*), and structure **B** as heterochiral (*PMP*)[2]). Both diastereoisomers exist in two enantiomers. In the above discussion, a racemic mixture of the homochiral diastereoisomer **A** has been assigned to the complex $[Fe_3(\mathbf{1})_2]^{6+}$. Transformation of one enantiomer into the other is only possible by decomplexation. This process is very slow for bis[terpyridine]iron complexes [27], and it should, therefore, be possible to separate the two enantiomers in solution.

The trinuclear Fe^{II} complex $[Fe_3(\mathbf{1})_2]Cl_6$ was loaded onto an ion-exchange resin (*Sephadex®-SP C-25*, 40–120 μ) and eluted with a solution of optically pure sodium (+)-tartratoantimonate(III) [28]. Elution of the diastereoisomeric salts could easily be followed due to their purple color, and finally two well-separated fractions were collected. These fractions contained two enantiomers of the complex as shown by their circular dichroism (CD) spectra (*Fig. 4*). The first fraction presents a negative band (negative *Cotton* effect) at 320 nm and two positive bands (positive *Cotton* effect) at 338 nm and 560 nm. The CD spectrum of the second fraction is exactly the mirror image of that of the first one. The two spectra may be assigned to the two helical enantiomers of the $[Fe_3(\mathbf{1})_2]^{6+}$ double helicate. These results confirm that the trinuclear complex consists of a racemic mixture of only one diastereoisomer.

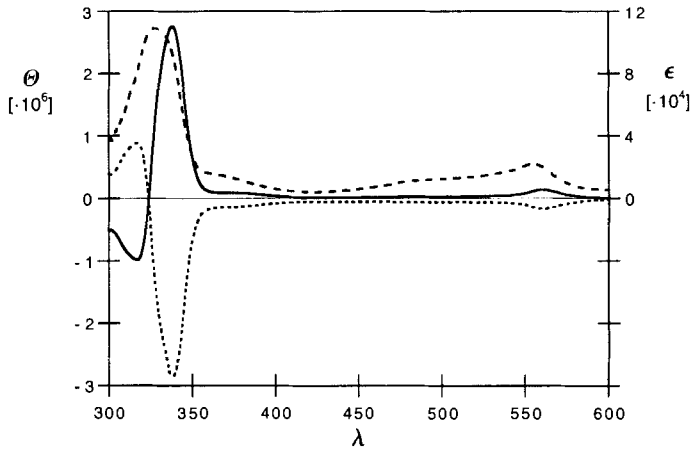


Fig. 4. *CD* (full and dotted curve) *and absorption spectra* (dashed curve) *of the two helical enantiomers of* $[Fe_3(\mathbf{1})_2]^{6+}$

The solutions did not loose any optical activity over six months at 5° and at 52° over seven weeks, indicating the much greater stability of the trinuclear supramolecular architecture, compared to the monometallic species [27].

The optically pure helicates $[Fe_3(\mathbf{1})_2]^{6+}$ open the way to further studies of the helical architecture by following their racemization process. The racemization might proceed by a step-by-step inversion of the individual metal centers. On the other hand, one might consider a chiral induction between the metal centers, so that the chirality of one center

[2]) The same stereochemical relationship has been discussed in detail for multinuclear double helicates formed from oligo(bipyridine) strands and Cu^I ions [26].

would determine the chirality of its neighbor. Steric hindrance and geometric restrictions by the ligand, as discussed above, are in favor of such an induction. To invert the helicity of the $[Fe_3(\mathbf{1})_2]^{6+}$ double helicate in this case, one ligand strand has to dissociate entirely. Comparison of the rate of racemization with the rate of ligand exchange should give indications for the different pathways.

3. Conclusion. – The formation of trinuclear double helicates $[Fe_3(\mathbf{1})_2]^{6+}$ by reaction of the linear tris[terpyridine] ligand **1** with Fe^{II} or Ni^{II} extends the series of helicates based on the complementarity of tridentate binding sites with octahedral coordination geometry. Only one diastereoisomer (as a racemate) is formed by this self-assembly process, and the resolution of the $[Fe_3(\mathbf{1})_2]^{6+}$ species into its optical antipodes shows the high stability of this trinuclear complex. Optically pure helicates provide means for studying chiral induction between the metal centers, as well as the mechanism of the self-assembly and wrapping/unwrapping processes. Multinuclear metal complexes, such as $[M_3(\mathbf{1})_2]^{6+}$, where the metal ions are linked by covalent bridges, are of interest for their photophysical and electrochemical properties, in particular, with respect to the interaction and communication between the subunits[3]).

Experimental Part

General. All commercially available chemicals employed were of reagent-grade and used without further purification. THF and toluene were distilled over Na/benzophenone. All reactions were carried out under Ar. Magnetic stirring was used. 2-Amino-5-methylpyridine was purchased from *Aldrich*. 2-Acetyl-5-methylpyridine (**2**) [19–21] and 2-(dimethylamino)ethenyl pyridin-2-yl-ketone (**5**) [18] were prepared by literature methods. M.p.: *Electrothermal* digital m.p. apparatus; no corrections. TLC: precoated plastic sheets *Polygram Sil G/UV*$_{254}$ and *Polygram Alox N/UV*$_{254}$ (*Macherey-Nagel*). Prep. column chromatography (CC): aluminium oxide (Al_2O_3; *Merck*, act. II–III, 0.063–0.200 mm). UV/VIS: *Cary 3*, λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$). CD: *Jobin Yvon CD6*, λ in nm (θ in $l \cdot mol^{-1} \cdot cm^{-1}$). FT-IR: *Perkin-Elmer*, $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR: *Bruker AC 200*, *Bruker AM 400*; δ in ppm relative to Me_4Si with residual solvent peak as standard, J in Hz. ^{13}C-NMR: broad-band decoupled. MS: *m/z* (rel. intensity), fast atom bombardment (FAB, positive mode) and electrospray (ES) were performed at the Laboratoire de Spectrométrie de Masse, Strasbourg. The microanalyses were done at the Service Central d'Analyses du CNRS, Lyon and the Centre Régional de Microanalyse, Université Pierre et Marie Curie, Paris.

2-(Dimethylamino)ethenyl Methylpyridin-2-yl Ketone (**4**). 2-Acetyl-5-methylpyridine (**2**; 4.51 g, 33.4 mmol) and dimethylformamid dimethyl acetal (4.77 g, 4.5 ml, 40 mmol) were dissolved in toluene (30 ml), and a catal. amout of TsOH was added. The flask was fitted with a *Dean-Stark* distillation apparatus and heated for 4 d to 100–110°. During this time, a brown solid precipitated. The mixture was concentrated under vacuum to a brown pasty solid. 10 ml of hexane were added and the solid was filtered off. After washing with hexane, 4.93 g (77%) of **4** were obtained. The compound was used without further purification in the next step. It can be recrystallized from toluene/cyclohexane. M.p. 110°. FT-IR (KBr): 1637*s*, 1579*s*, 1550*s*, 1433*s*, 1352*s*, 1235*m*, 1115*m*, 1055*s*, 1029*m*, 905*m*, 790*m*, 600*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.34 (*s*, Me of Py); 2.99 (br. *s*, MeN); 3.15 (br. *s*, MeN); 6.42 (*d*, J = 12.7, COCH); 7.58 (*dm*, J = 8.0, H–C(4)); 7.88 (*d*, J = 12.7, C*H*NMe_2); 8.04 (*d*, J = 8.0, H–C(3)); 8.44 (*d*, J = 2.1, H–C(6)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 18.6 (Me); 37.5 (Me); 45.1 (Me); 91.3, 121.8, 135.5, 137.2, 148.8, 154.0, 154.6 (C(py), C=C); 187.1 (C=O). FAB-MS: 191 (100, $[M + 1]^+$). Anal. calc. for $C_{11}H_{14}N_2O$ (190.24): C 69.45, H 7.42, N 14.73; found: C 69.47, H 7.32, N 14.74.

5,5″-Dimethyl-2,2′:6′,2″-terpyridine (**6**). *t*-BuOK (3.25 g, 28.7 mmol) was added to a stirred soln. of **2** (1.94 g, 14.3 mmol) in THF (80 ml). After 2 h, **4** (2.73 g, 14.4 mmol) was added and stirring continued for 7 h. Then, NH_4OAc (10.8 g, 0.14 mol) and AcOH (40 mol) were added, and the mixture was refluxed for 2.5 h. The mixture was concentrated under vacuum to a black oil, which was taken up in 80 ml of H_2O and basified by addition of Na_2CO_3. The soln. was extracted with 300 ml of CH_2Cl_2 in small portions. The combined org. phases were dried (Na_2SO_4) and evaporated to dryness. The solid residue was taken up in toluene and filtered through *Celite*. The filtrate was then evaporated and purified by CC (Al_2O_3, CH_2Cl_2/hexane 1:1). After one recrystallization from

[3]) For example, the complex $\{[Ru(terpy)]_3(\mathbf{1})\}^{6+}$ was prepared and its photophysical properties were studied [29].

toluene, 995 mg (26%) of **6** were obtained. The yield can be increased to 35% by further recrystallization of the filtrate. M.p. 177°. FT-IR (KBr): 2917*w*, 1592*m*, 1558*s*, 1484*s*, 1444*s*, 1376*m*, 1258*w*, 1217*w*, 1150*w*, 1134*m*, 1101*w*, 1080*w*, 1025*s*, 994*w*, 868*w*, 814*vs*, 771*w*, 755*s*, 674*w*, 639*w*, 587*w*, 521*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.41 (*s*, 2 Me); 7.65 (*dd*, J = 8.0, 2.2, H–C(4), H–C(4″)); 7.92 (*t*, J = 7.8, H–C(4′)); 8.38 (*d*, J = 7.8, H–C(3′), H–C(5′)); 8.48–8.52 (*m*, H–C(3), H–C(6), H–C(3″), H–C(6″)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 18.4 (Me); 120.3, 120.6, 133.3, 137.3, 137.7, 149.5, 153.8, 155.4 (arom. C). FAB-MS: 262 (100, $[M + 1]^+$). Anal. calc. for $C_{17}H_{15}N_3$ (261.33): C 78.13, H 5.79, N 16.08; found: C 77.92, H 5.86, N 16.02.

5-Methyl-2,2′:6′,2″-terpyridine (7). The preparation was analogous to that of **6**, starting with **2** and **5**. M.p. 79–80°. FT-IR (KBr): 1577*m*, 1562*s*, 1489*w*, 1471*m*, 1450*m*, 1430*s*, 1265*w*, 1123*w*, 1101*m*, 1077*m*, 1025*m*, 991*w*, 848*w*, 824*m*, 781*vs*, 753*vs*, 699*w*, 652*m*, 621*w*, 511*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.41 (*s*, Me); 7.32 (*ddd*, J = 7.5, 4.8, 1.1, H–C(5″)); 7.64 (*dm*, J = 7, H–C(4)); 7.85 (*td*, J = 7.7, 1.8, H–C(4″)); 7.94 (*t*, J = 7.9, H–C(4′)); 8.42 (*dd*, J = 7.8, 1.0, H–C(3′), H–C(5′)); 8.49–8.53 (*m*, H–C(6), H–C(3)); 8.62 (*dd*, J = 8.0, 1.0, H–C(3″)); 8.70 (*dm*, J = 7, H–C(6″)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 18.4 (Me); 120.4, 120.7, 121.2, 123.7, 133.4, 136.8, 137.4, 137.9, 149.1, 149.6, 153.8, 155.4, 155.5, 156.4 (arom. C). FAB-MS: 248 (100, $[M + 1]^+$). Anal. calc. for $C_{16}H_{13}N_3$ (247.30): C 77.71, H 5.30, N 16.99; found: C 77.23, H 5.30, N 16.67.

5,5″-Bis(bromomethyl)-2,2′:6′,2″-terpyridine (**8**). A soln. of **6** (454 mg, 1.74 mmol), *N*-bromosuccinimid (NBS; 1.55 g, 8.69 mmol) and benzoyl peroxide (70%, 65 mg) in CCl_4 (50 ml) was heated to reflux for 0.5 h. The hot soln. was then filtered and the solid washed with 50 ml of CCl_4. The filtrate was concentrated to 20 ml under vacuum. A white solid precipitated, which was isolated and redissolved in 50 ml of CH_2Cl_2. The soln. was extracted twice with $Na_2S_2O_3$ (0.5M in H_2O) to remove remaining NBS, dried (Na_2SO_4), and evaporated to dryness. Recrystallization from CCl_4 yielded 165 mg of **8**. The combined filtrates containing **8** togother with polybrominated products were evaporated under vacuum and redissolved in 50 ml of CH_2Cl_2. At −78°, diisobutylaluminium hydride (DIBAL-H, 1M in CH_2Cl_2) was added in small portions, until TLC analysis did not reveal any polybrominated products. The reaction was quenched with 20 ml aq. NH_4Cl and 50 ml of H_2O. The mixture was filtered through *Celite* and washed with CH_2Cl_2. The phases were separated and the org. soln. was washed twice with 100 ml of H_2O, then dried (Na_2SO_4), and evaporated under vacuum. Purification by a short column of Al_2O_3 and recrystallization from CCl_4 yielded another 186 mg of product **8** (total yield 48%). M.p. 188°. FT-IR (KBr): 1594*s*, 1551*vs*, 1451*s*, 1395*m*, 1238*w*, 1025*m*, 816*vs*, 761*s*, 679*m*, 641*m*, 618*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.57 (*s*, CH_2Br); 7.90 (*dd*, J = 7.2, 2.3, H–C(4), H–C(4″)); 7.96 (*t*, J = 7, H–C(4′)); 8.46 (*d*, J = 7.8, H–C(3′), H–C(5′)); 8.59 (*d*, J = 7.3, H–C(3), H–C(3″)); 8.71 (*d*, J = 2, H–C(6), H–C(6″)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 29.8 (CH_2Br); 121.2, 121.5, 133.8, 137.6, 138.1, 149.4, 154.9, 156.1 (arom. C). FAB-MS: 420 (100, $[M + 1]^+$). Anal. calc. for $C_{17}H_{13}Br_2N_3$ (419.13): C 48.72, H 3.13, N 10.03; found: C 48.41, H 3.02, N 9.81.

5,5″-Bis[2-(2,2′:6′,2″-terpyridin-5-yl)ethyl]-2,2′:6′,2″-terpyridine (**1**). Freshly prepared lithium diisopropylamide (LDA; 0.67 mmol in 2 ml) was added to a soln. of **7** (165 mg, 0.67 mmol) in THF (2 ml) at −78°. After 10 min, the flask was placed in an ice-bath (0°), and a soln. of **8** (70 mg, 0.17 mmol) in 4 ml of THF was added dropwise. The mixture was stirred at 0° for 2 h. 20 ml of aq. NH_4Cl and 50 ml of H_2O were added, and the mixture was extracted with $CHCl_3$ (4 × 15 ml). The combined org. extracts were dried (Na_2SO_4) and evaporated under vacuum. The solid was redissolved in hot $CHCl_3$/MeOH 9:1 (2 ml) and the soln. layered with Et_2O (1 ml). The compound **1** precipitates as an off-white solid (92 mg, 72%). M.p. 234–236°. FT-IR (KBr): 2925*w*, 1584*m*, 1559*s*, 1484*w*, 1451*s*, 1430*s*, 1390*m*, 1262*w*, 1102*w*, 1026*w*, 992*w*, 817*m*, 787*m*, 763*s*, 655*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.10 (*s*, 4 CH_2); 7.29–7.35 (*m*, 2 H–C(5″) of terminal terpyridines); 7.58–7.63 (*m*, 2 H–C(4) of terminal terpyridines, 2 H–C(4) of central terpyridine); 7.80–8.00 (*m*, 2 H–C(4′) and 2 H–C(4″) of terminal terpyridines, H–C(4′) of central terpyridine); 8.30–8.75 (*m*, 18 arom. H); assignment by comparison with precursors. ^{13}C-NMR (50.3 MHz, $CDCl_3$): 34.5 (CH_2); 120.9, 121.2, 123.8, 136.3, 136.9, 137.0, 137.9, 149.2, 149.4, 154.6, 155.3 (arom. C). FAB-MS: 753 (100, $[M + 1]^+$). Anal. calc. for $C_{49}H_{37}N_9O \cdot H_2O$ (751.90): C 76.44, H 5.11, N 16.37; found: C 76.15, H 5.04, N 16.29.

Bis{5,5″-bis[2-(2,2′:6′,2″-terpyridin-5-yl)ethyl]-2,2′:6′,2″-terpyridine}-triiron(II) Hexafluorophosphate ($[Fe_3(\mathbf{1})_2](PF_6)_6$). $FeCl_2 \cdot 4\ H_2O$ (20.0 mg, 0.099 mmol) was added to **1** (50.0 mg, 0.066 mmol) suspended in ethyleneglycol (5 ml). The mixture was heated to 175°. It turned slowly deep purple as the compounds dissolved. After 12 h, the mixture was cooled to r.t. and dropped into an aq. soln. of NH_4PF_6 (600 mg in 15 ml). The purple precipitate was isolated by centrifugation and washed with H_2O. It was redissolved three times in acetone and precipitated from Et_2O to obtain 82 mg (98%) of the complex $[Fe_3(\mathbf{1})_2](PF_6)_6$ as a purple powder. M.p. > 300°. UV/VIS (MeCN): 278 ($9.5 \cdot 10^4$); 327 ($1.1 \cdot 10^5$); 554 ($2.3 \cdot 10^4$). FT-IR (KBr): 3426*s* (br.), 1654*w*, 1608*w*, 1560*w*, 1507*w*, 1453*s*, 1251*w*, 840*vs*, 778*m*, 558*s*. ^{1}H-NMR (400 MHz, CD_3CN): 2.45–2.55 (*m*, 4 CH_2); 6.02 (*d*, J = 1.7, 2 H–C(6) of central terpyridine); 6.08 (*d*, J = 1.96, 2 H–C(6) of terminal terpyridines); 6.95–7.01 (*m*, 2 H–C(5″), 2 H–C(6″) of terminal terpyridines); 7.35 (*dd*, J = 8.32, 1.96, 2 H–C(4) of terminal terpyridines, H–C(4) of central terpyridine); 7.83 (*td*, J = 7.84, 1.72, 2 H–C(4″) of terminal terpyridines); 8.26 (*d*, J = 8.04, 2 H–C(3) of terminal

terpyridines, H–C(3) of central terpyridine); 8.40 (*d*, $J = 8.04$, 2 H–C(3″) of terminal terpyridines); 8.72 (*t*, $J = 8.04$, 2 H–C(4′) of terminal terpyridines); 8.79 (*t*, $J = 7.3$, H–C(4′) of central terpyridine); 8.85 (*d*, $J = 8.04$, 2 H–C(5′) of terminal terpyridines); 8.93 (*d*, $J = 7.8$, 2 H–C(3′) of central terpyridine); 8.94 (*d*, $J = 7.8$, 2 H–C(3′) of terminal terpyridines); assignment by 2D-COSY NMR. ES-MS: 1125.23 (5, $[Fe_3(\mathbf{1})_2](PF_6)_4^{2+}$); 701.46 (35, $[Fe_3(\mathbf{1})_2](PF_6)_3^{3+}$); 489.69 (85, $[Fe_3(\mathbf{1})_2](PF_6)_2^{4+}$); 362.44 (40, $[Fe_3(\mathbf{1})_2](PF_6)^{5+}$); 277.65 (100, $[Fe_3(\mathbf{1})_2](PF_6)^{6+}$). FAB-MS: 2396 (87, $[Fe_3(\mathbf{1})_2(PF_6)_5]^+$); 2251 (100, $[Fe_3(\mathbf{1})_2(PF_6)_4]^+$); 2106, (27, $[Fe_3(\mathbf{1})_2(PF_6)_3]^+$). Anal. calc. for $C_{98}H_{74}F_{36}Fe_3N_{18}P_6 \cdot 5\ H_2O$ (2541.12): C 44.77, H 3.22, N 9.58; found: C 44.83, H 3.22, N 9.73.

Optical Resolution of $[Fe_3(\mathbf{1})_2]^{6+}$. A column of 12-mm diameter was packed with 10 g of *Sephadex-SP-C25* swollen in H_2O. 29 mg of $[Fe_3(\mathbf{1})_2]Cl_6$, dissolved in 1 ml of H_2O, were loaded onto the column and eluted with a 0.3M soln. of sodium (+)-tartratoantimonate(III). The compound separated into two fractions, which were collected and analyzed by CD measurements. These aq. solns. were concentrated under vacuum to a viscous liquid, and NH_4PF_6 was added. The solns. were extracted with MeCN. The org. solns. were dropped into aq. NH_4PF_6 to precipitate the optically active complexes $[Fe_3(\mathbf{1})_2](PF_6)_6$, which were isolated by centrifugation and dried in a dessicator over $CaCl_2$.

Bis{5,5″-bis[2-(2,2′:6′,2″-terpyridin-5-yl)ethyl]-2,2′:6′,2″-terpyridine}-trinickel(II) Perchlorate ($[Ni_3(\mathbf{1})_2](ClO_4)_6$). The Ni^{II} complex was prepared in the same way as the Fe^{II} complex and isolated as the perchlorate or the hexafluorophosphate salt. M.p. > 300°. FAB-MS: 2177 (80, $[Ni_3(\mathbf{1})_2](ClO_4)_5^+$); 2077 (100, $[Ni_3(\mathbf{1})_2](ClO_4)_4^+$); 1977 (40, $[Ni_3(1)_2](ClO_4)_3^+$). FT-IR (KBr): 1602*w*, 1562*w*, 1479*w*, 1454*m*, 1323*w*, 1251*w*, 1145*m*, 1108*s*, 1088*vs*, 1043*s*, 883*m*, 861*w*, 786*w*, 626*m*. UV/VIS (MeCN): 246 ($1.0 \cdot 10^5$); 274 ($1.0 \cdot 10^5$); 328 ($9.0 \cdot 10^4$); 341 ($9.5 \cdot 10^4$); 552 (290); 774 (170). Anal. calc. for $C_{98}H_{74}F_{36}N_{18}Ni_3P_6 \cdot 2\ H_2O$ (2585.72): C 45.52, H 3.04, N 9.75; found: 45.57, H 3.28, N 10.05.

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