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Self-Assembly of Dinuclear Double- and Triple-Stranded Helicates from Bis(bipyridine) Ligands Derived from Tröger's Base Analogues

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Based on the rigid and V-shaped structure of Tröger's base, several dissymmetrical bis(bipyridine) ligands with both rigid and flexible spacer units have been synthesized, and their self-assembly to double- and triple-stranded helicates upon coordination to late transition metal ions has been investigated by NMR spectroscopic and ESI mass spectrometric means.

Introduction

An increasing amount of attention has been paid to the chemistry of Tröger's base (Figure 1), a chiral tertiary amine first synthesized in 1887 by Julius Tröger,[1] in the last few years.[2] This is mainly due to its attractive rigid and V-shaped core, which makes it an ideal building block for the design of concave receptor molecules like the beautiful examples reported by Wilcox[3] and Goswami[4] that have been used for the recognition of neutral molecules, such as adenin, menthol or dicarboxyclic acids, in the 1980s and 1990s. However, the true renaissance is also a consequence of the fact that a direct access to symmetrically 2,8-dihalo-substituted analogues of Tröger's base (Figure 1) was established only a few years ago by Wärnmark.[5] Since then, subsequent advancement of this methodology has allowed the introduction of halogens into almost every position of the two aromatic rings.[6] Alternative methods, however, also allow the formation of monohalogenated analogues[7] that could be used to synthesize molecular torsion balances.[7b,8] Especially dibromo- or diiodo-substituted derivatives are valuable precursors for the synthesis of larger architectures with extended V-shaped cores by various cross-coupling strategies. Consequently, numerous new derivatives have been synthesized by Sonogashira,[9a,10] Suzuki,[9] Kumada,[5] Negishi, Stille[9c] cross-coupling reactions, Hartwig–Buchwald aminations,[9d] or Pd-catalyzed cyanations[9b] in the last couple of years by us and other research groups.

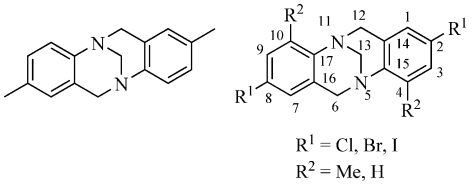

Figure 1. Tröger's base (left) and 2,8-dihalo-substituted analogues of Tröger's base (right).

Very recent applications of Tröger's base derivatives include the preparation of potentially restrictive α-amino acid based scaffolds.[10b] However, Tröger's base derivatives have also very interesting stereochemical properties, since they are dissymmetric and therefore chiral molecules that have even been demonstrated to be useful chiral auxiliaries for the enantioselective synthesis of aziridines.[11] Thus, these compounds attracted our interest as C_2-symmetrical building blocks for the construction of chiral ligand structures to control the stereochemistry of metal centers of dinuclear helical coordination compounds (helicates) in a diastereoselective manner, an issue that has seen a tremendous development recently.[12–14] Hence, we synthesized four racemic ligands bearing either 2-pyridylmethanimine or 2,2′-bipyridine metal-chelating units (Figure 2) that indeed underwent diastereoselective self-assembly to dinuclear double-stranded helicates upon coordination to silver(I) and copper(I) ions,[15] which has been only the second example of the formation of late transition metal ion complexes derived from ligands whose geometry is defined by the shape of Tröger's base so far.[16]

Except for ligand **2** (Figure 2) the bis(bipyridine) ligands synthesized before bear very rigid spacers like ethynylene or butadiynylene functions which lead to well-defined structures of the double-stranded dinuclear helicates upon coordination to silver(I) or copper(I) ions bearing chiral cavities, potentially useful for molecular recognition studies as a

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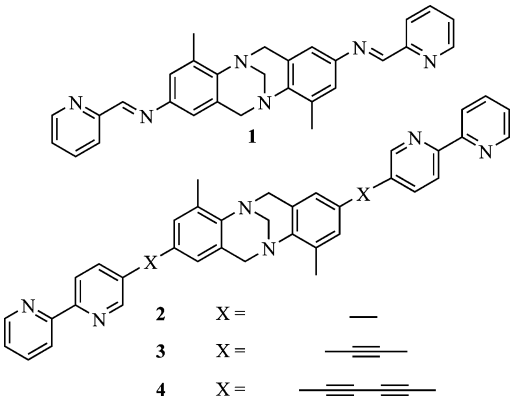


Figure 2. Ligands **1**–**4** bearing 2,2′-bipyridine or 2-pyridylmethanimine moieties as metal-chelating units.

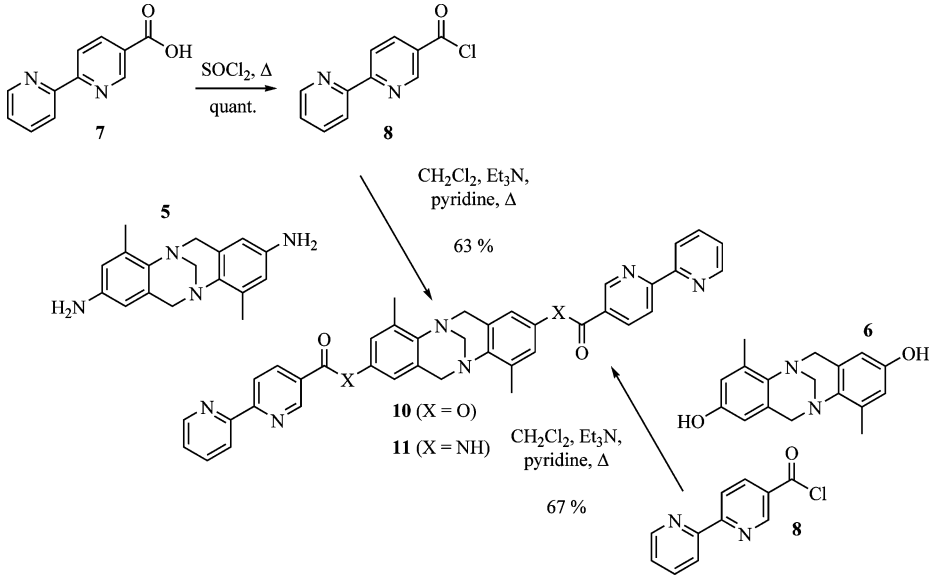
long-term goal. Thus, we wondered whether the diastereoselectivity of the self-assembly observed for the formation of dinuclear D_2-symmetrical double-stranded helicates can also be achieved by using ligands with even more flexible spacers, such as ester or amide functions. In addition, we wanted to address the question, whether the formation of triple-stranded helicates from both the rigid and the flexible ligands, which would bear an even more interesting – because closed – cavity, is also possible by using other ions as zinc(II) or iron(II) that prefer (or at least allow) an octahedral coordination by three bipyridine units and whether these processes are also diastereoselective.

Results and Discussion

In order to study the issue of diastereoselectivity of helicate self-assembly processes, it is even advantageous to use racemic ligands rather than enantiomerically pure ones. This sounds surprising at a first glance but doing so also allows the formation of additional heteroleptic complexes that incorporate ligands of different configuration that are also diastereomers of the homoleptic complexes formed from the optically pure ligands. Thus, even more information can be gained from the investigations of racemic ligands because one can also address the question whether the self-asssembly process proceeds under some kind of self-sorting of the enantiomeric forms of the ligands in the assemblies. Hence, we prepared and studied racemic ligands in this account rather than optically pure ones, since the elucidation of the stereoselectivity was the primary goal.

The introduction of ester and amide bonds into the Tröger's base core leading to analogous ligands with respect to **1**–**4** can be achieved by esterification or amide formation of 2,8-diamino- and 2,8-dihydroxy precursors **5** and **6** of Tröger's base with 2,2′-bipyridine-5-carboxylic acid (**7**) or its corresponding acyl chloride **8**, respectively. Compound **7** can be prepared from methyl 2,2′-bipyridine-5-carboxylate (**9**), which is readily available by a modified Negishi cross-coupling strategy as we have recently reported,[17] by simple cleavage of its ester bond (Scheme 1). Carboxylic acid **7** can be transformed in situ into the much more reactive acyl chloride **8** by refluxing of **7** in thionyl chloride.[14k] The desired amide- and ester-bridged ligands **10** and **11** can subsequently be synthesized in good yields by adding diamino- or dihydroxy-substituted precursors **5** or **6**, dissolved in a mixture of dichloromethane, triethylamine, and pyridine, to a solution of **8** in dichloromethane (Scheme 1). The synthesis of disubstituted precursors **5** and **6** of Tröger's base has also been previously reported by us.[9a,15] With the successful formation of ligands **10** and **11**, we have extended the scope of bis(bipyridine) ligands derived from 2,8-disubstituted analogues of Tröger's base to ligands with flexible and more extensive spacer units than the C–C single bond of ligand **2** (Figure 2).

We then explored the coordination behavior of the two ligands **10** and **11** towards copper(I) and silver(I) ions which



Scheme 1. Synthesis of amide- and ester-bridged ligands **10** and **11**.

typically prefer a tetrahedral coordination geometry by four donor atoms. As observed previously for ligands **1**–**4**, characteristic color changes took place (yellow for Ag^+ and brown for Cu^+ complexes) upon addition of solutions of the metal salts to our ligands in a 1:1 ratio, which provided a first hint for the formation of the desired metal coordination compounds. The ^1H NMR spectra of the complexes derived from ligands **10** and **11** are shown in Figures 3 and 4.

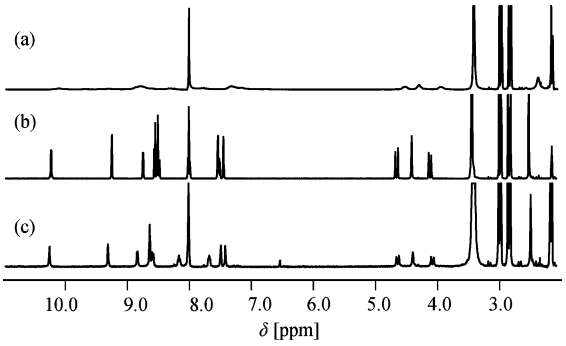


Figure 3. ^1H NMR complexation studies of **10** in [D_7]DMF/CD_3CN (3:1) at 298 K. (a) **10** + $[Cu(CH_3CN)_4]BF_4$ (1:1). (b) **10**. (c) **10** + $[Ag(CH_3CN)_2]BF_4$ (1:1).

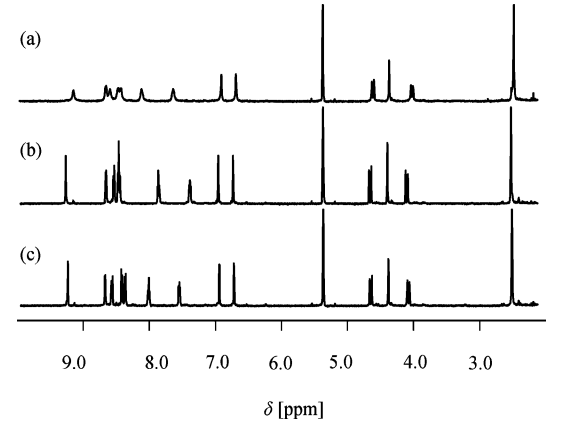


Figure 4. ^1H NMR complexation studies of **11** in CD_2Cl_2/CD_3CN (3:1) 298 K. (a) **11** + $[Cu(CH_3CN)_4]BF_4$ (1:1). (b) **11**. (c) **11** + $[Ag(CH_3CN)_2]BF_4$ (1:1).

In all cases, relatively broad signals were obtained for the copper(I) complexes, which could indicate the formation of oligomeric and polymeric rather than discrete dinuclear aggregates or a very dynamic behavior (of a single discrete species) on the NMR time scale. The same observation was made previously for ligands **1**–**4**[15] as well as for BINOL-derived ligands[14n] and could be proven to be due to dynamic ligand-exchange phenomena of the desired discrete dinuclear helicates. The spectra of the silver(I) complexes, however, are well-resolved and show only one set of sharp and significantly shifted signals compared to those of the free ligands. These shifts observed upon addition of the metal salts indicate a successful formation of the metal complexes.

To exclude the occurence of possible oligomeric or polymeric species, ESI-MS experiments were carried out, which clearly indicated the exclusive formation of dinuclear complexes in all four cases. The ESI mass spectrum of $[Cu_2(\mathbf{11})_2](BF_4)_2$ is shown in Figure 5.

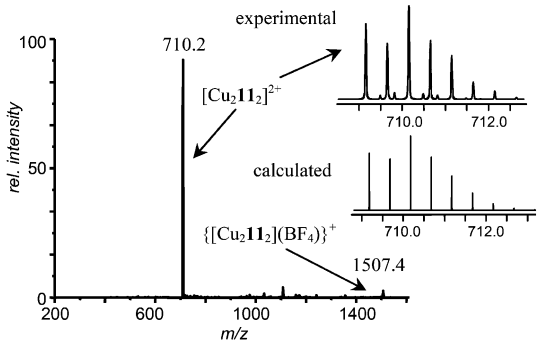


Figure 5. Positive-ESI mass spectrum of a solution of $[Cu_2(\mathbf{11})_2](BF_4)_2$ in CH_2Cl_2.

Together with the results obtained from the MS analysis, however, some further profound conclusions can be drawn from the interpretation of the ^1H NMR spectra: Because the number of signals of the free ligands is equal to the number of signals of their complexes, one can conclude that the two halves of the ligands are magnetically still equivalent in the newly formed aggregates, which is only possible if the two metal centers of each assembly have the same configuration [(Δ,Δ) or (Λ,Λ)]. Since **10** and **11** were used in racemic form, one can also exclude the formation of heteroleptic complexes with differently configured ligand strands that would also give rise to a more complex spectrum of at least double the number of signals. Furthermore, (Δ,Δ)- and (Λ,Λ)-configured helicates are diastereomers, and it is very unlikely that all the proton signals of these two diastereomers should be isochronic by coincidence. Thus, it is reasonable to conclude that the self-assembly process of racemic ligands **10** and **11** to double-stranded helicates is also completely diastereoselective as observed for **1**–**4**, resulting in racemic pairs of dinculear D_2-symmetric silver(I) and copper(I) complexes with equally configured metal centers.

Unfortunately, we have not yet succeeded in growing suitable single crystals for X-ray crystal-structure analysis to definitely assign the relative stereochemistry of our aggregates. However, ROESY NMR measurements have also proven to be a valuable tool to investigate the stereochemistry of this kind of aggregates in solution. Thus, we carried out ROESY NMR experiments with the silver(I) complexes of **10** and **11** to elucidate the relative orientation of the bipyridine unit with regard to the Tröger's base core of the aggregates. Unfortunately, but somehow expected and already observed for C–C single-bond-bridged ligand **2** (due to a twist of the aromatic rings), no unambiguous assignments can be made for ligands **10** and **11** which bear flexible ester or amide functions, respectively (due to the flexibility of the spacer groups). ROE contacts of the amide proton or the protons of the aromatic rings of the Tröger's base and the adjacent bipyridine protons with respect to the amide or ester function can be observed to both protons of

the Tröger's base core in these cases (see Supporting Information for the ^{1}H ROESY NMR spectra), which do not allow a definite assignment. However, the (Λ,Λ)-configured silver(I) complexes derived from the (5*S*,11*S*) enantiomers of **11** and also **10** [or their (Δ,Δ)-(5*R*,11*R*)-configured enantiomers] are more likely from modeling structures,[18] because the carbonyl functions are oriented farthest away from the bipyridine nitrogen atoms, and the ROE contact between 23-H and 9-H is more distinct than that between 23-H and 7-H (Figure 6), but these indications need to be confirmed in due course.

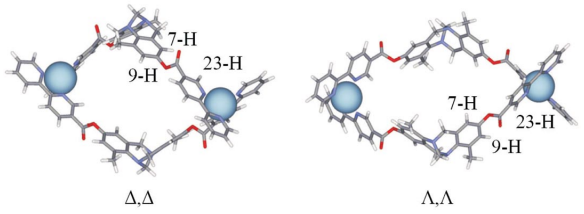


Figure 6. PM3-minimzed structures of (Δ,Δ)-{Ag_2[(5*S*,11*S*)-**11**]$_2$}$^{2+}$ and (Λ,Λ)-{Ag_2[(5*S*,11*S*)-**11**]$_2$}$^{2+}$.

Having successfully established the diastereoselective formation of double-stranded D_2-symmetric helicates from rather flexible Tröger's base derived ligands, we took our concept a step further and started to investigate the construction of triple-stranded helical metal complexes as the next logical step by applying other metal ions, which prefer (or at least allow) an octahedral coordination geometry by three bipyridine units such as iron(II) or zinc(II) ions. Therefore, we explored the coordination behavior of ligands **10** and **11** as well as of ligands **2** and **3** towards these metal ions.[19]

First, we studied the complexation behavior of our ligands towards zinc(II) ions. Zinc(II) has a d^{10} configuration and thus cannot gain any additional stabilization from a certain ligand field. However, zinc(II) has been found to form mainly hexacoordinated metal complexes in an octahedral coordination geometry in solution when treated with chelating ligands like 1,10-phenanthrolines or 2,2′-bipyridines, although fourfold coordination in a tetrahedral fashion has also been observed by us when D-isomannide is used as structure-defining element.[20] According to this, the use of Zn^{2+} may – in general – result in both species, double-stranded helicates and triple-stranded helicates, due to its "chameleon" character.[21] Therefore, the self-assembly of the zinc(II) complexes and also the stereoselectivity of these processes should be quite sensitive to the preorganization of the bis(bipyridine) ligand's conformation to ensure the formation of dinuclear coordination compounds.

Mixing of 3 equiv. of ligands **2**, **3**, **10**, and **11** with 2 equiv. of $Zn(BF_4)_2{\cdot}6.5H_2O$ or $Zn(ClO_4)_2{\cdot}6H_2O$ as zinc(II) salts resulted in the instant formation of yellow solutions, and the ESI MS analyses clearly showed the formation of discrete triple-stranded dinuclear coordination compounds as shown in Figure 7 for the complexes of ligand **2**. Encouraged by these results, we then turned to NMR spectroscopy to obtain further insight into the aggregates formed. The ^{1}H NMR spectra, however, revealed an initially surprising and disappointing behavior of our ligands, because they clearly demonstrate that the formation of the triple-stranded complexes is not (diastereo)selective any more and results in a dynamic mixture of coordination compounds in most cases. Figure 8 shows the ^{1}H NMR spectra of ligand **2** and its corresponding mixture with Zn^{II} ions.

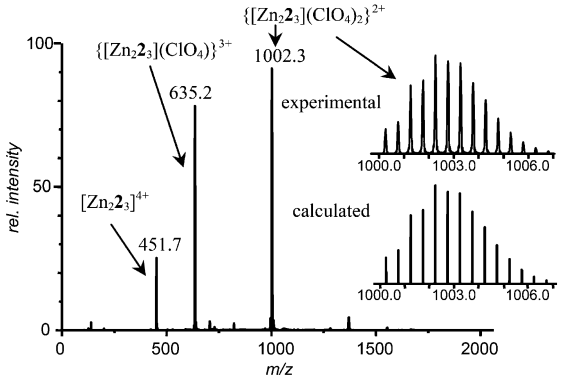


Figure 7. Positive-ESI mass spectrum of a solution of a 2:3 mixture of $[Zn(ClO_4)_2]{\cdot}6H_2O$ and **2** in CH_2Cl_2/CH_3CN.

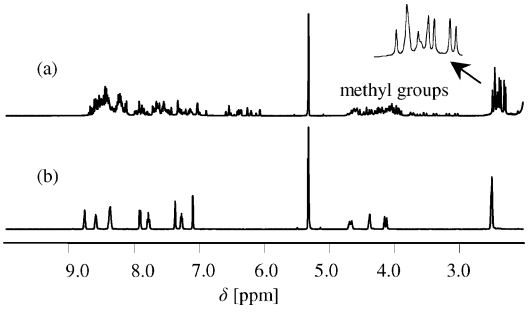


Figure 8. ^{1}H NMR complexation studies of **2** in CD_2Cl_2/CD_3CN (3:1). (a) **2** + $[Zn(BF_4)_2]{\cdot}6.5H_2O$ (3:2). (b) **2**.

In case of the complexes of **2**, a closer look at the methyl groups of the Tröger's base core revealed the formation of (at least) seven different species. The self-assembly process is not diastereoselective any more, and the formation of at least seven species clearly indicates the formation of homoleptic but also heteroleptic complexes, because homoleptic complexes with equally configured ligands would give rise to only four different methyl resonances for the three possible diastereomeric species [(Δ,Δ), (Λ,Λ), (Δ,Λ)]. Since signal overlap is very likely in this complex mixture, it seems reasonable to assume that all six possible diastereomers (as pairs of enantiomers, of course) are present in solution. This is in sharp contrast to the observations made for copper(I) and silver(I). Thus, it seems that the conformation of ligands based on this special Tröger's base core is not really well preorganized to build triple-stranded helicates. Thus, strain is induced into the ligand's skeleton, which seems to level out the energetic differences between the diasteromeric homoleptic but also the heteroleptic diastereomers and finally results in an almost complete loss of stereoselectivity of the self-assembly process. This is in agreement with ob-

servations that we made earlier with bis(catecholato) ligands bearing the 2,8-functionalized Tröger's base core where the self-assembly processes of dinuclear triple-stranded titanium(IV) complexes were also found to be almost non-diastereoselective.[22]

After this somehow disappointing result, we turned our attention to the coordination studies with iron(II) ions. Iron(II) is a classical d^6-electron system that is known to form thermodynamically very stable (although not necessarily kinetically stable) low-spin complexes with chelating N-donor ligands, like 2,2′-bipyridines or 1,10-phenanthrolines, thus gaining maximum stabilization by the optimum $t_{2g}{}^6$ electron configuration due to the ligand field. Thus, the formation of octahedrally coordinated metal centers is highly favored, and triple-stranded species usually form even if the ligand's conformation has to be bent to some extent to ensure the formation of coordination compounds. Upon addition of a solution of iron(II) ions {2 equiv., either as $[Fe(BF_4)_2]\cdot 6H_2O$ or as $[Fe(SO_4)]\cdot 7H_2O$} to each of the ligands (3 equiv.), an immediate change to an intensive red color could be observed in all cases, which is characteristic for low-spin (biypridine)Fe^{II} complexes. ESI mass spectrometric analyses of the complexes' solution were performed, which clearly proved the formation of triple-stranded aggregates, because only signals of the desired dinuclear helicates could be detected [Figure 9 shows the ESI mass spectrum of $(Fe_2\mathbf{2}_3)(BF_4)_4$].

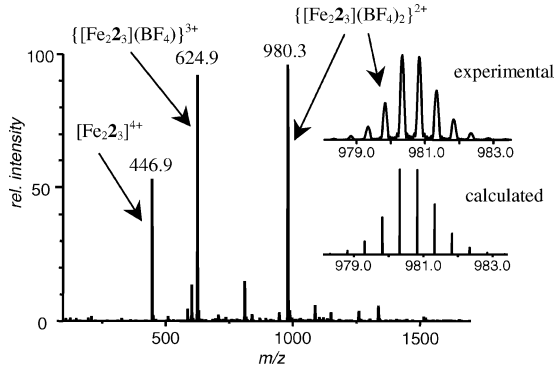


Figure 9. Positive-ESI mass spectrum of a solution of $[Fe_2\mathbf{2}_3](BF_4)_4$ in CH_2Cl_2.

Figure 10 shows the representative ^1H NMR complexation studies of ligands **2** and **3** towards Fe^{II}. As in the case of copper(I) ions, the signals of the Fe^{II} complexes are relatively broad compared to the those of the free ligand due to their kinetic lability as we already had found out in earlier studies with a corresponding BINOL-based ligand.[14n] Another characteristic feature of the iron(II) complexes is the fact, that the shifts observed upon formation of the coordination compound are relatively small compared to those of the other metal ions investigated. Still, as in the cases of the double-stranded copper(I) and silver(I) complexes, one can conclude that the number of signals is the same as in the case of the free ligands and thus only homoleptic dinuclear coordination compounds with equally configured metal centers seem to be formed [see Figure 11 for the PM3-minimized structures of the diastereomeric (Δ,Δ)-$\{Fe_2[(5S,11S)\text{-}\mathbf{2}]_3\}^{4+}$ and (Λ,Λ)-$\{Fe_2[(5S,11S)\text{-}\mathbf{2}]_3\}^{4+}$ complexes].

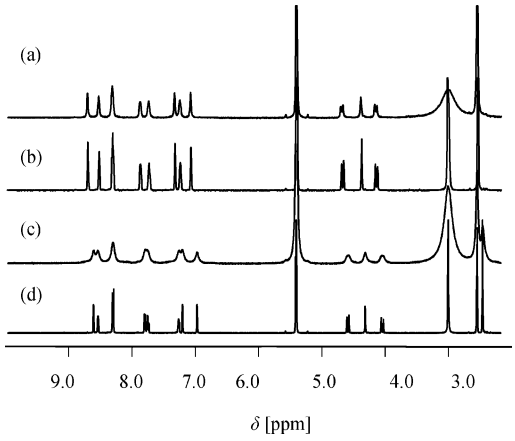


Figure 10. ^1H NMR complexation studies of **2** and **3** in CD_2Cl_2/[D_6]DMSO (3:1), 298 K. (a) **2** + $[Fe(SO_4)\cdot 7H_2O]$ (3:2). (b) **2**. (c) **3** + $[Fe(BF_4)_2\cdot 6H_2O]$ (3:2). (d) **3**.

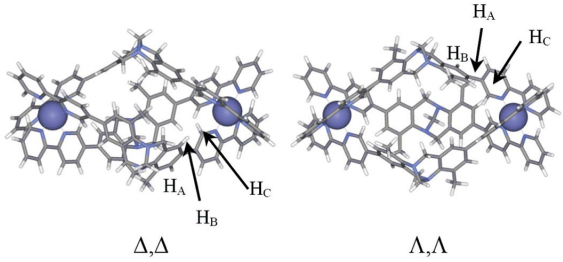


Figure 11. PM3-minimzed structures of (Δ,Δ)-$[Fe_2\{(5S,11S)\text{-}\mathbf{2}\}_3]^{4+}$ and (Λ,Λ)-$[Fe_2\{(5S,11S)\text{-}\mathbf{2}\}_3]^{4+}$.

Unfortunately, ROESY NMR experiments allowed no unambiguous assignment of the stereochemistry of the metal centers, either because the twist of the aromatic rings of the Tröger's base and the bipyridine core via the C–C single bond in **2** results in ROE signals of H_A to both H_B and H_C of both diasteromers (Figure 11), or due to the dynamic behavior and precipitation of the other metal complexes (which prevented low-temperature measurements in order to slow down the dynamic behavior).

However, the diastereoselectivity itself is a very interesting result, because it shows how sensible these processes are to subtle changes. Although the molecular structure of the ligands seems to be not ideal for the formation of triple-stranded dinuclear coordination compounds, the energy necessary to adopt this unfavorable arrangement is obviously compensated by a substantial amount of ligand-field stabilization energy in the case of iron(II) leading to a selective formation of only a single metallo supramolecular aggregate. Zinc(II) complexes, however, that do not experience any special stabilization by a certain ligand field cannot compensate this lack of conformational preorganization, and thus the self-assembly processes rather give rise to complex mixtures of aggregates.

Conclusions

We have shown that racemic bis(bipyridine) ligands **10** and **11** bearing flexible amide or ester groups self-assemble to double-stranded homoleptic D_2-symmetric helicates in a diastereoselective manner upon coordination of silver(I) and copper(I) ions. The configuration of the newly formed stereogenic metal centers is completely controlled by the configuration of the Tröger's base core, although the stereochemistry of the metal centers could not be unambiguously assigned on the basis of ROESY NMR studies. Nevertheless, the diastereoselectivity is in agreement with the results observed for ligands **1**, **2**, **3**, and **4** and proves that the conformation of bis(bipyridyl) ligands bearing a 2,8-functionalized Tröger's base core is well preorganized to ensure selective self-assembly of diastereomerically pure (racemic) dinuclear double-stranded coordination compounds. However, complexation studies of ligands **2**, **3**, **10**, and **11** with zinc(II) ions clearly demonstrated that the ligands' conformation is obviously not well preorganized for the diastereoselective formation of triple-stranded helicates, because the respective self-assembly processes only yielded complex mixtures of dinuclear coordination compounds. This again is in agreement with the results obtained in complexation studies of corresponding bis(catecholato) ligands towards titanium(IV), also bearing the 2,8-functionalized Tröger's base core. The lack of preorganization can, however, be compensated by the choice of a suitable metal ion like iron(II), because this d^6 system can gain a substantial amount of stabilization energy by arranging the ligands in an octahedral coordination sphere around energetically favorable t_{2g}^6-configured low-spin metal centers. Thus, the additional stabilization through the ligand field, not found in the case of d^{10}-configured ions like zinc(II), seems to ensure the diastereoselective formation of racemic triple-stranded dinuclear iron(II) helicates. Having elucidated the diastereoselectivity of the self-assembly processes of ligands derived from 2,8-substituted Tröger's base analogues, we are currently developing resolution methods to prepare the ligands in enantiomerically pure form in order to investigate the molecular recognition behavior of the optically pure self-assembled helical aggregates with suitable guest molecules or ions.

Experimental Section

General Information: All reactions were performed under argon using standard Schlenk techniques and oven-dried glassware prior to use. TLC was performed on aluminium TLC plates with silica gel 60 F_{254} from Merck. Detection was done by UV light (254 and 366 nm). Products were purified by column chromatography on silica gel 60 (70–230 mesh) from Merck. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX 500 spectrometer (300 K, 500.1 and 125.8 MHz), a Bruker AM 400 spectrometer (298 K, 400.1 MHz and 100.6 MHz), or a Bruker Avance 300 (298 K, 300.1 MHz and 75.5 MHz). ^{1}H NMR chemical shifts are reported on the δ scale (ppm) relative to residual non-deuterated solvent as internal standard. ^{13}C NMR chemical shifts are reported on the δ scale (ppm) relative to deuterated solvent as internal standard. Signals were assigned on the basis of ^{1}H,^{13}C HMQC and HMBC NMR experiments. Mass spectra were recorded with a Finnigan MAT 212 spectrometer with data system MMS-ICIS (EI), a Finnigan MAT 95 spectrometer with data system DEC-Station 5000 (CI, isobutene; HiRes-EI; FD) or an A.E.I. MS-50 spectrometer (EI; HiRes-EI). ESI mass spectra were recored with a Bruker APEX IV FT mass spectrometer. Melting points were measured with a hot-stage microscope SM-Lux from Leitz and are not corrected. Elemental analyses were carried out with a Fisons Instrument EA1108 or a Heraeus Vario EL. Unfortunately, fluorine-containing samples cannot be analysed by this equipment because fluorine damages the GC column used in these instruments. Thus, the metal complexes with tetrafluoroborate counterions could not be analysed in this way. Therefore, we provide copies of the ^{1}H NMR spectra for all dinuclear complexes and ^{13}C NMR spectra of the silver(I) complex of **11** (see Supporting Information if not already shown above) as well as the results of mass spectra for all metal complexes obtained by ESI-FTICR-MS measurements. Isotopic peaks given always refer to the most intense isotopic peaks. These experimental values are in accordance with the calculated ones in all cases (within one decimal). ^{13}C NMR spectra of the copper(I) and iron(II) complexes do show very broad, badly resolved peaks due to dynamical ligand exchange processes that do not allow a proper assignment. Unfortunately, the precipitation of the complexes at lower temperatures prevented the measuring at significantly lower temperatures. Molecular-modeling studies were carried out with Spartan Pro (Wavefunction). All solvents used for the synthesis of **5** and **6** were dried, distilled and stored under argon according to standard procedures. All chemicals were used as received from commercial sources. Methyl 2,2′-bipyridine-5-carboxylate[20] (**9**), 2,8-diamino-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine[15] (**6**), 2,8-dihydroxy-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine[9a] (**5**), 2,8-bis(2,2′-bipyridinyl-5-ylethynyl)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine[15] (**3**), 2,8-bis(2,2′-bipyridinyl-5-yl)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine[15] (**2**) and 2,2′-bipyridine-5-carboxylic acid[20] (**7**) were prepared according to published procedures. Numbering of the ^{1}H and ^{13}C is shown in Figure 12.

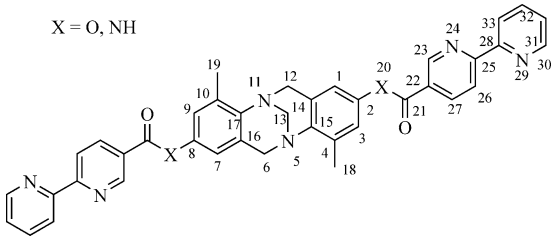


Figure 12. Numbering of the ^{1}H and ^{13}C nuclei.

2,8-Bis(2,2′-bipyridin-5-ylcarbonylamino)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (10): 2,2′-Bipyridine-5-carboxylic acid (**7**) (200 mg, 1.00 mmol, 2.4 equiv.) was suspended in thionyl chloride (12 mL), and the resulting suspension was refluxed for 16 h. After ca. 2 h, **7** was completely dissolved. Thionyl chloride was removed in vacuo and the remaining solid dried in vacuo for 5 h. Dichloromethane (15 mL) was added to dissolve the product 2,2′-bipyridine-5-carbonyl chloride (**8**). Compound **6** (117 mg, 0.42 mmol) was dissolved in dichloromethane (10 mL), Et_3N (3 mL) and pyridine (3 mL), and the resulting solution was added dropwise to the dissolved carbonyl chloride **8** at room temp. After refluxing for 16 h, the reaction mixture was cooled and filtered through Celite. The filter was rinsed with ethyl acetate (100 mL) and 2-propanol (30 mL), the filtrate washed with water

(7 × 100 mL), and the aqueous layers were extracted with ethyl acetate and dried with Na_2SO_4. The solvents were evaporated, and the crude product was suspended in a mixture of toluene/methanol (9:1) and refluxed for 1 h. The suspension was cooled and stored at –24 °C for 20 h. The precipitate was collected. Yield: 148 mg (0.23 mmol, 51%), m.p. >250 °C. ^{1}H NMR (500.1 MHz, [D$_6$]-DMSO): δ = 2.39 (s, 6 H, 18-H, 19-H), 3.96 (d, ^2J = 17.0 Hz, 2 H, 6*endo*-H, 12*endo*-H), 4.27 (s, 2 H, 13-H), 4.54 (d, ^2J = 17.0 Hz, 2 H, 6*exo*-H, 12*exo*-H), 7.33 (d, $^4J_{1,3}$ = 1.8 Hz, 2 H, 1-H, 7-H), 7.42 (d, 2 H, $^4J_{1,3}$ = 1.8 Hz, 3-H, 9-H), 7.50 (ddd, $^3J_{30,31}$ = 4.7 Hz, $^3J_{31,32}$ = 7.5 Hz, $^4J_{31,33}$ = 1.1 Hz, 2 H, 31-H, 31′-H), 7.98 (ddd, $^3J_{32,33}$ = 7.7 Hz, $^3J_{31,32}$ = 7.7 Hz, $^4J_{30,32}$ = 1.7 Hz, 2 H, 32-H, 32′-H), 8.40 (dd, $^3J_{26,27}$ = 8.2 Hz, $^4J_{23,27}$ = 2.2 Hz, 2 H, 27-H), 8.44 (d, $^3J_{32,33}$ = 7.7 Hz, 2 H, 33-H, 33′-H), 8.50 (dd, $^3J_{26,27}$ = 8.2 Hz, $^5J_{23,26}$ = 0.6 Hz, 2 H, 26-H, 26′-H), 8.73 (ddd, $^3J_{30,31}$ = 4.7 Hz, $^4J_{30,32}$ = 1.7 Hz, $^5J_{30,33}$ = 0.6 Hz, 2 H, 30-H, 30′-H), 9.15 (dd, $^4J_{23,27}$ = 2.2 Hz, $^5J_{23,26}$ = 0.6 Hz, 2 H, 23-H, 23′-H), 10.29 (s, 2 H, NH) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 16.9 (C-18, C-19), 54.7 (C-6, C-12), 67.2 (C-13), 116.3 (C-1, C-7), 119.9 (C-26, C-26′), 121.1 (C-3, C-9, C-33, C-33′), 124.8 (C-31, C-31′), 128.2 (C-14, C-16), 130.4 (C-22, C-22′), 132.5 (C-4, C-10), 134.2 (C-2, C-8), 136.5 (C-27, C-27′), 137.5 (C-32, C-32′), 141.9 (C-15, C-17), 148.5 (C-23, C-23′), 149.5 (C-30, C-30′), 154.4 (C-28, C-28′), 157.3 (C-25, C-25′), 163.3 (C-21, C-21′) ppm. MS (EI): *m*/*z* (%) = 644.3 (100) $[C_{39}H_{32}N_8O_2]^{+\cdot}$. HR-MS (EI): calcd. 644.2648, found 644.2651. $C_{39}H_{32}N_8O_2\cdot H_2O$ (644.72 + 18.02): calcd. C 70.68, H 5.17, N 16.91; found C 70.90, H 5.07, N 16.90.

2,8-Bis(2,2′-bipyridin-5-ylcarbonyloxy)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (11): 2,2′-Bipyridine-5-carboxylic acid (**7**) (190 mg, 0.95 mmol, 2.4 equiv.) was suspended in thionyl chloride (12 mL), and the resulting suspension was refluxed for 16 h. After ca. 2 h, **7** was completely dissolved. Thionyl chloride was removed in vacuo and the remaining solid dried in vacuo for 5 h. Dichloromethane (15 mL) was added to dissolve the product 2,2′-bipyridin-5-ylcarbonyl chloride (**8**). Compound **5** (111.7 mg, 0.40 mmol) was dissolved in dichloromethane (20 mL), Et_3N (3 mL), and pyridine (3 mL), and the resulting solution was added dropwise to the dissolved carbonyl chloride **8** at room temp. After refluxing for 16 h, the reaction mixture was cooled and filtered through Celite. The filter was rinsed with dichloromethane (100 mL), the filtrate washed with water (7 × 100 mL), and the aqueous layers were xtracted with dichloromethane and dried with Na_2SO_4. The solvents were evaporated, and the crude product was purified by column chromatography [toluene/THF (9:1) + 5% Et_3N; R_f = 0.26]. Yield: 140 mg (0.27 mmol, 67%), m.p. 124–126 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.45 (s, 6 H, 18-H, 19-H), 4.02 (d, ^2J = 17.0 Hz, 2 H, 6*endo*-H, 12*endo*-H), 4.34 (s, 2 H, 13-H), 4.63 (d, ^2J = 17.0 Hz, 2 H, 6*exo*-H, 12*exo*-H), 6.72 (s, 2 H, 1-H, 7-H), 6.96 (s, 2 H, 3-H, 9-H), 7.37 (ddd, $^3J_{30,31}$ = 5.5 Hz, $^3J_{31,32}$ = 7.6 Hz, $^4J_{31,33}$ not resolved, 2 H, 31-H, 31′-H), 7.86 (ddd, $^3J_{32,33}$ = 8.2 Hz, $^3J_{31,32}$ = 7.6 Hz, $^4J_{30,32}$ = 1.6 Hz, 2 H, 32-H, 32′-H), 8.50 (dd, $^3J_{26,27}$ = $^3J_{32,33}$ = 8.2 Hz, 4 H, 27-H, 27′-H, 33-H, 33′-H), 8.56 (dd, $^3J_{26,27}$ = 8.2 Hz, $^4J_{23,27}$ not resolved, 2 H, 26-H, 26′-H), 8.72 (d, $^3J_{30,31}$ = 4.3 Hz, 2 H, 30-H, 30′-H), 9.38 (s, 2 H, 23-H, 23′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 17.1 (C-18, C-19), 55.0 (C-6, C-12), 67.4 (C-13), 117.0 (C-1, C-7), 120.6 (C-26, C-26′), 121.9 (C-33, C-33′)*, 122.0 (C-3, C-9)*, 124.6 (C-31, C-31′), 125.2 (C-22, C-22′), 129.2 (C-14, C-16), 134.9 (C-4, C-10), 137.1 (C-32, C-32′), 138.5 (C-27, C-27′), 143.9 (C-15, C-17), 146.4 (C-2, C-8), 149.4 (C-30, C-30′), 150.9 (C-23, C-23′), 154.9 (C-28, C-28′), 159.9 (C-25, C-25′), 164.2 (C-21, C-21′) ppm; *assignment not confirmed due to peak overlap. MS (EI): *m*/*z* (%) = 646.2 (100) $[C_{39}H_{30}N_6O_4]^{+\cdot}$. HR-MS (EI): calcd. 646.2329, found 646.2332. $C_{39}H_{30}N_6O_4\cdot 4H_2O\cdot C_6H_5CH_3$ (646.69 + 72.06 + 92.14): calcd. C 68.13, H 5.72, N 10.36; found C 67.98, H 5.74, N 10.08.

Preparation and Characterization of the Metal Complexes: Ligands **2**, **3**, **10**, and **11** were dissolved in CD_2Cl_2 or [D$_7$]DMF (2 mL), and $[Ag(CH_3CN)_2]BF_4$, $[Cu(CH_3CN)_4]BF_4$, $[Zn(BF_4)_2]\cdot 6.5H_2O$, $[Zn(ClO_4)_2]\cdot 6H_2O$, $[Fe(BF_4)_2]\cdot 6H_2O$, or $[Fe(SO_4)]\cdot 6.5H_2O$ were dissolved in CD_3CN or [D$_6$]DMSO (1 mL). Equimolar amounts of the two solutions (600 μL of the ligand, 200 μL of the metal salt) were combined in case of the double-stranded complexes and analyzed by NMR spectroscopic methods [only the ^{1}H and ^{13}C NMR data of the silver(I) complexes are listed below due to relatively broad signals in case of the copper(I) and iron(II) complexes and the complex mixtures obtained in the case of zinc(II) complexes]. Diluted solutions of the complexes were analyzed by ESI MS methods afterwards. A 3:2 stochiometry (ligand/metal salt) was applied in case of the triple-stranded complexes.

$[Ag_2(\mathbf{10})_2](BF_4)_2$: Compound **10** (12.6 mg, 19.6 μmol) was dissolved in [D$_7$]DMF (2 mL), and 600 μL (3.8 mg, 5.88 μmol) was filled into an NMR tube. $[Ag(CH_3CN)_2]BF_4$ (8.1 mg, 29.4 μmol) was dissolved in CD_3CN (1 mL), and 200 μL (1.6 mg, 5.9 μmol) of this solution was combined with the solution of **10** in the tube. Upon mixing, an immediate colour change from colourless to yellow could be observed. ^{1}H NMR {500.1 MHz, [D$_7$]DMF/CD_3CN (3:1), reference DMF}: δ = 2.42 (s, 6 H,18-H, 19-H), 4.03 (d, ^2J = 17.0 Hz, 2 H, 6*endo*-H, 12*endo*-H), 4.35 (s, 2 H, 13-H), 4.59 (d, ^2J = 17.0 Hz, 2 H, 6*exo*-H, 12*exo*-H), 7.41 (s, 2 H, 1-H, 7-H), 7.48 (s, 2 H, 3-H, 9-H), 7.71 (ddd, $^3J_{30,31}$ = 3.9 Hz, $^3J_{31,32}$ = 7.6 Hz, $^4J_{31,33}$ not resolved, 2 H, 31-H, 31′-H), 8.20 (ddd, $^3J_{31,32}$ = 7.6 Hz, $^3J_{32,33}$ = 8.2 Hz, $^4J_{30,32}$ = 1.6 Hz, 2 H, 32-H, 32′-H), 8.60 (d, $^3J_{26,27}$ = 8.2 Hz, 2 H, 26-H, 26′-H), 8.65–8.66 (m, 4 H, 27-H, 27′-H, 33-H, 33′-H) 8.86 (s, 2 H, 30-H, 30′-H), 9.34 (s, 2 H, 23-H, 23′-H), 10.28 (s, 2 H, NH) ppm. ^{13}C NMR {125.8 MHz, [D$_7$]DMF/CD_3CN (3:1), reference [D$_7$]DMF}: δ = 17.1 (C-18, C-19), 55.8 (C-6, C-12), 68.2 (C-13), 116.9 (C-1, C-7), 121.8 (C-3, C-9), 122.4 (C-33, C-33′), 123.6 (C-26, C-26′), 126.5 (C-31, C-31′), 129.2 (C-14, C-16), 132.4 (C-22, C-22′), 133.7 (C-4, C-10), 135.2 (C-2, C-8), 138.3 (C-27, C-27′), 139.6 (C-32, C-32′), 143.1 (C-15, C-17), 150.5 (C-23, C-23′), 151.4 (C-30, C-30′), 152.8 (C-28, C-28′) ppm; signals of the quaternary carbon atoms C-21/C-21′ and C-25/C-25′ could neither be detected in the ^{13}C NMR nor in the HMBC spectra because of the low signal intensity due to the low solubility of the complex. MS (ESI): *m*/*z* (%) = 752.2 (100) $[Ag_2\mathbf{10}_2]^{2+}$/$[Ag\mathbf{10}]^+$ {1:2}, 1074.8 (6) $[Ag_2\mathbf{10}_3]^+$, 1397.5 (4) $[Ag\mathbf{10}_2]^+$.

$[Cu_2(\mathbf{10})_2](BF_4)_2$: Compound **10** (12.6 mg, 19.6 μmol) was dissolved in [D$_7$]DMF (2 mL), and 600 μL (3.8 mg, 5.88 μmol) was filled into an NMR tube. $[Cu(CH_3CN)_4]BF_4$ (9.3 mg, 29.4 μmol) was dissolved in CD_3CN (1 mL), and 200 μL (1.9 mg, 5.88 μmol) of this solution was combined with the solution of **10** in the tube. Upon mixing, an immediate change from colourless to brown could be observed. MS (ESI): *m*/*z* (%) = 708.2 (100) $[Cu_2\mathbf{10}_2]^{2+}$, 973.3 (10) $\{[Cu_4\mathbf{10}_4]BF_4\}^{3+}$, 1503.4 (4) $\{[Cu_2\mathbf{10}_2]BF_4\}^+$.

$[Ag_2(\mathbf{11})_2](BF_4)_2$: Compound **11** (5.0 mg, 7.68 μmol) was dissolved in of CD_2Cl_2 (2 mL), and 600 μL (1.5 mg, 2.30 μmol) was filled into an NMR tube. $[Ag(CH_3CN)_2]BF_4$ (3.2 mg, 11.5 μmol) was dissolved in CD_3CN (1 mL), and 200 μL (0.6 mg, 2.3 μmol) of this solution was combined with the solution of **11** in the tube. Upon mixing, an immediate change from colourless to yellow could be observed. ^{1}H NMR {500.1 MHz, CD_2Cl_2/CD_3CN (3:1), reference CH_2Cl_2}: δ = 2.40 (s, 6 H, 18-H, 19-H), 4.00 (d, ^2J = 17.0 Hz, 2 H, 6*endo*-H, 12*endo*-H), 4.31 (s, 2 H, 13-H), 4.58 (d, ^2J = 17.0 Hz, 2 H, 6*exo*-H, 12*exo*-H), 6.70 (d, $^4J_{1,3}$ = 2.2 Hz, 2 H, 1-H, 7-H), 6.92 (s, 2 H, 3-H, 9-H), 7.54 (ddd, $^3J_{30,31}$ = 4.4 Hz, $^3J_{31,32}$ = 7.6 Hz,

$^4J_{31,33}$ not resolved, 2 H, 31-H, 31′-H), 8.02 (ddd, $^3J_{31,32}$ = 7.6 Hz, $^3J_{32,33}$ = 8.2 Hz, $^4J_{32,34}$ not resolved, 2 H, 32-H, 32′-H), 8.38 (d, $^3J_{32,33}$ = 8.2 Hz, 2 H, 33-H, 33′-H), 8.43 (d, $^3J_{26,27}$ = 8.2 Hz, 2 H, 26-H, 26′-H), 8.58 (dd, $^3J_{26,27}$ = 8.2 Hz, $^4J_{23,27}$ = 1.7 Hz, 2 H, 27-H, 27′-H), 8.69 (d, $^3J_{30,31}$ = 4.4 Hz, 2 H, 30-H, 30′-H), 9.27 (s, 2 H, 23-H, 23′-H) ppm. ^{13}C NMR {125.8 MHz, CD_2Cl_2/CD_3CN (3:1), reference CD_2Cl_2}: δ = 16.9 (C-18, C-19), 55.2 (C-6, C-12), 67.5 (C-13), 117.9 (C-1, C-7),121.9 (C-3, C-9)*, 122.0 (C-26, C-26′)*, 123.2 (C-33, C-33′), 126.1(C-31, C-31′), 126.6 (C-22, C-22′), 129.5 (C-14, C-16), 135.1 (C-4, C-10), 138.8 (C-32, C-32′), 139.7 (C-27, C-27′), 144.1 (C-15, C-17),146.5 (C-2, C-8),150.7 (C-30, C-30′), 151.5 (C-23, C-23′), 152.3 (C-28, C-28′), 157.1 (C-25, C-25′), 163.6 (C-21, C-21′) ppm; *assignment not confirmed due to peak overlap. MS (ESI): *m/z* (%) = 754.2 (100) $[Ag_2\mathbf{11}_2]^{2+}$/$[Ag\mathbf{11}]^+$ {1:2}, 1175.2 (3) $[Ag\mathbf{11}_2]^+$, 1595.3 (3) $\{[Ag_2\mathbf{11}_2]BF_4\}^+$.

$[Cu_2(\mathbf{11})_2](BF_4)_2$: Compound **11** (5.0 mg, 7.68 μmol) was dissolved in CD_2Cl_2 (2 mL), and 600 μL (1.5 mg, 2.30 μmol) was filled into an NMR tube. $[Cu(CH_3CN)_4]BF_4$ (3.6 mg,11.5 μmol) was dissolved in CD_3CN (1 mL), and 200 μL (0.7 mg, 2.3 μmol) of this solution was combined with the solution of **11** in the tube. Upon mixing, an immediate change from colourless to brown could be observed. MS (ESI): *m/z* (%) = 710.2 (100) $[Cu_2\mathbf{11}_2]^{2+}$, 1108.3 (4) $[Cu_2\mathbf{11}_3]^{2+}$, 1507.4 (4) $\{[Cu_2\mathbf{11}_2]BF_4\}^+$.

$[Zn_2\mathbf{10}_3](ClO_4)_4$: Compound **10** (11.4 mg, 17.6 μmol) was dissolved in $[D_7]$DMF (2 mL), and 600 μL (3.4 mg, 5.30 μmol) was filled into an NMR tube. $[Zn(ClO_4)_2]\cdot 6H_2O$ (6.6 mg, 17.6 μmol) was dissolved in CD_3CN (1 mL), and 200 μL (1.3 mg, 3.52 μmol) of this solution was combined with the solution of **10** in the tube. Upon mixing, an immediate change from colourless to yellow could be observed. MS (ESI): *m/z* (%) = 516.2 (100) $[Zn_2\mathbf{10}_3]^{4+}$, 699.9 (80) $\{[Zn_2\mathbf{10}_3]Cl\}^{3+}$,# 721.2 (70) $\{[Zn_2\mathbf{10}_3]ClO_4\}^{3+}$, 914.9 (20) $\{[Zn_2\mathbf{10}_4]Cl\}^{3+}$,# 936.3 (20) $\{[Zn_2\mathbf{10}_4]ClO_4\}^{3+}$,* 1067.3 (15) $\{[Zn_2\mathbf{10}_3]Cl_2\}^{2+}$,# 1099.3 (15) $\{[Zn_2\mathbf{10}_3](ClO_4)Cl\}^{2+}$,# 1131.3 (15) $\{[Zn_2\mathbf{10}_3](ClO_4)_2\}^{2+}$; # in some cases residual chloride ions from the calibration substance were found to be able to substitute weakly coordinating perchlorate ions during the ESI-MS experiment, *$\{[Zn_2\mathbf{10}_4]ClO_4\}^{3+}$ is most probably a gas-phase adduct of the triple-stranded complex and a free ligand strand.

$[Zn_2\mathbf{11}_3](ClO_4)_4$: Compound **11** (11.4 mg, 17.6 μmol) was dissolved in of CD_2Cl_2 (2 mL), and 600 μL (3.4 mg, 5.30 μmol) was filled into an NMR tube. $[Zn(ClO_4)_2]\cdot 6H_2O$ (6.6 mg, 17.6 μmol) was dissolved in CD_3CN (1 mL), and 200 μL (1.3 mg, 3.52 μmol) of this solution was combined with the solution of **11** in the tube. Upon mixing, an immediate change from colourless to yellow could be observed. MS (ESI): *m/z* (%) = 517.7 (10) $[Zn_2\mathbf{11}_3]^{4+}$, 723.2 (100) $\{[Zn_2\mathbf{11}_3]ClO_4\}^{3+}$, 811.1 (9) $\{[Zn_2\mathbf{11}_2](ClO_4)_2\}^{2+}$, 1134.2 (20) $\{[Zn_2\mathbf{11}_3](ClO_4)_2\}^{2+}$.

$[Fe_2\mathbf{2}_3](SO_4)_2$ and $[Fe_2\mathbf{2}_3](BF_4)_4$: Compound **2** (9.8 mg, 17.6 μmol) was dissolved in CD_2Cl_2 (2 mL), and 600 μL (3.7 mg, 5.30 μmol) was filled into an NMR tube. $[Fe(SO_4)_2]\cdot 6.5H_2O$ (4.9 mg, 17.6 μmol) was dissolved in $[D_6]$DMSO (1 mL), and 200 μL (1.0 mg, 3.52 μmol) of this solution was combined with the solution of **2** in the tube. Upon mixing, an immediate change from colourless to intensive red could be observed. $[Fe(BF_4)_2]\cdot 6H_2O$ was used as Fe^{II} source for the ESI mass spectrometric investigation. MS (ESI): *m/z* (%) = 446.9 (60) $[Fe_2\mathbf{2}_3]^{4+}$, 624.9 (90) $\{[Fe_2\mathbf{2}_3]BF_4\}^{3+}$, 811.0 (8) $\{[Fe_2\mathbf{2}_4]BF_4\}^{3+}$, 980.4 (100) $\{[Fe_2\mathbf{2}_3](BF_4)_2\}^{2+}$.

$[Fe_2\mathbf{3}_3](SO_4)_2$ and $[Fe_2\mathbf{3}_3](BF_4)_4$: Compound **3** (10.7 mg, 17.6 μmol) was dissolved in CD_2Cl_2 (2 mL), and 600 μL (3.3 mg, 5.30 μmol) was filled into an NMR tube. $[Fe(SO_4)_2]\cdot 6.5H_2O$ (4.9 mg, 17.6 μmol) was dissolved in $[D_6]$DMSO (1 mL), and 200 μL (1.0 mg, 3.52 μmol) of this solution was combined with the solution of **3** in the tube. Upon mixing, an immediate change from colourless to intensive red could be observed. $[Fe(BF_4)_2]\cdot 6H_2O$ was used as Fe^{II} source for the ESI mass spectrometric investigation. MS (ESI): *m/z* (%) = 482.9 (30) $[Fe_2\mathbf{3}_3]^{4+}$, 650.2 (30) $\{[Fe_2\mathbf{3}_3]F\}^{3+}$ {loss of BF_3}, 672.9 (100) $\{[Fe_2\mathbf{3}_3]BF_4\}^{3+}$, 1052.8 (20) $\{[Fe_2\mathbf{3}_3](BF_4)_2\}^{2+}$.

$[Fe_2\mathbf{10}_3](SO_4)_2$ and $[Fe_2\mathbf{10}_3]Cl_4$: Compound **10** (12.6 mg, 19.6 μmol) was dissolved in $[D_7]$DMF (2 mL), and 600 μL (3.8 mg, 5.88 μmol) was filled into an NMR tube. $[Fe(SO_4)_2]\cdot 6.5H_2O$ (5.5 mg, 19.6 μmol) was dissolved in $[D_6]$DMSO (1 mL), and 200 μL (1.1 mg, 3.92 μmol) of this solution was combined with the solution of **10** in the tube. Upon mixing, an immediate change from colourless to intensive red could be observed. $[FeCl_2]$ was used as Fe^{II} source for the ESI mass spectrometric investigation. MS (ESI): *m/z* (%) = 511.4 (5) $[Fe_2\mathbf{10}_3]^{4+}$, 693.6 (10) $\{[Fe_2\mathbf{10}_3]Cl\}^{3+}$, 1058.3 (100) $\{[Fe_2\mathbf{10}_3]Cl_2\}^{2+}$.

$[Fe_2\mathbf{11}_3](SO_4)_2$ and $[Fe_2\mathbf{11}_3](BF_4)_4$: Compound **11** (11.4 mg, 17.6 μmol) was dissolved in CD_2Cl_2 (2 mL), and 600 μL (3.4 mg, 5.30 μmol) was filled into an NMR tube. $[Fe(SO_4)_2]\cdot 6.5H_2O$ (4.9 mg, 17.6 μmol) was dissolved in $[D_6]$DMSO (1 mL), and 200 μL (1.0 mg, 3.52 μmol) of this solution was combined with the solution of **11** in the tube. Upon mixing, an immediate change from colourless to intensive red could be observed. $[Fe(BF_4)_2]\cdot 6H_2O$ was used as Fe^{II} source for the ESI mass spectrometric investigation. MS (ESI): *m/z* (%) = 512.9 (80) $[Fe_2\mathbf{11}_3]^{4+}$, 690.2 (100) $\{[Fe_2\mathbf{11}_3]F\}^{3+}$ {loss of BF_3}, 712.9 (20) $\{[Fe_2\mathbf{11}_3]BF_4\}^{3+}$, 1112.8 (20) $\{[Fe_2\mathbf{11}_3](BF_4)_2\}^{2+}$.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of the zinc(II) and iron(II) complexes of **3**, **10**, and **11** not illustrated in the text. ^{1}H ROESY NMR spectra of the silver(I) complexes of **10** and **11**.

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