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Messages in Molecules: Ligand/Cation Coding and Self-Recognition in a Constitutionally Dynamic System of Heterometallic Double Helicates

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Abstract: Double helicates are known to exhibit self-recognition characteristics determined by the coordination geometry of the metal involved as well as by the topicity of the ligands. Combining tridentate (terpyridine, T) or bidentate (bipyridine, B) subunits in a tritopic strand affords a set of ligands able to assemble by pairs to form double helicates, homo- or heterostranded, homo- or heterotopic, depending on the coordination properties of the metals involved. The four ligand strands, BBB, TTT, BBT, and TBT form constitutionally dynamic sets of double helicates with the metal ions Cu^{I}, Cu^{II}, and Zn^{II}; these helicates correspond to the correct coding of the BB, BT, and TT pairs for tetra-, penta-, and hexacoordinate Cu^{I}, Cu^{II}, and Zn^{II} cations, respectively.

Keywords: helical structures · molecular information · self-assembly · self-recognition · supramolecular chemistry

Introduction

Supramolecular chemistry has been instrumental in the perception of chemistry as an information science. Indeed, the controlled assembly of well-defined supramolecular entities rests on the storage of molecular information within the covalently bound components as appropriate arrays of interaction sites, and its processing through recognition algorithms based on specific noncovalent interactional patterns. The program is thus molecular and its operation is supramolecular.[1–3]

These features are prevalent in arrays of hydrogen-bonding sites as present in nucleic acid strands, but they also apply to metallosupramolecular chemistry. Here, the instructions are given by the nature, number, and arrangement of the coordination subunits and their reading/processing is performed by means of the recognition algorithm defined by the coordination properties of the metal ion(s).[1–3] Indeed a great variety of metallosupramolecular architectures has been generated by self-organization processes implementing these programming principles.[4]

Among them, helical metal complexes, the helicates, have served as benchmarks for such studies,[4a–c] since their initial description.[5a] They are based on polytopic ligand strands that entwine themselves around a one-dimensional array of metal cations, double helicates being particularly well-studied systems. Depending on the nature of the coordination subunits and of the metal ions, homo-[5] or heterostranded[6] double helicates are obtained, and combined subunit/cation selectivity[7–9] is observed. Of special interest is the occurrence of self-recognition (self-sorting),[9] in which mixtures of ligands and metal ions in dynamic coordination equilibrium undergo spontaneous selection of the correct strands and metal ions, yielding the helicates expected on the basis of the coordination program and indicating the robustness of the instructions.

Such self-selection amounts to a dynamic exploration of the diversity space of the various possible combinations, ultimately generating the thermodynamically favored one. It

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displays self-assembly by a reversible process performing selection of the correct partner(s). As such, it has been of special significance in the emergence of dynamic combinatorial chemistry,[10] the reversible covalent sector of constitutional dynamic chemistry,[11] which also encompasses the supramolecular domain, the entities of which are dynamic by essence due to the lability of noncovalent connections, as in metallosupramolecular species such as the helicates.

Coding and selection in helicate self-assembly: Coding and selection in the self-organization of metallosupramolecular species are based upon 1) information storage at the molecular level, in the coordination subunits (number, nature, positioning of the interaction sites); 2) information processing at the supramolecular level, by metal-ion binding through specific algorithms defined by the coordination features of the cations (tetra-, penta-, hexacoordinate; tetrahedral, trigonal-bipyramidal, square-pyramidal, octahedral, etc.); and 3) correspondence between the subunits and the metal cations, which determines the mode of ligand/cation assembly. In the case of helicates, the order of the helicate (double, triple, or quadruple stranded) as well as its homo- or heterostranded nature depend on the denticity of the coordination subunit (bidentate or tridentate) and the coordination number (four, five, or six) of the metal ion; these factors define the number of subunits surrounding a given coordination center (Figure 1). A sequence of coordination subunits may be considered as a *codon*, a ligand strand consisting of one or several such codons.

The helicates may be of different types depending on whether the strands and coordination centers are the same or different. Thus, double helicates may be homostranded–homotopic, homostranded–heterotopic, heterostranded–homotopic, or heterostranded–heterotopic.

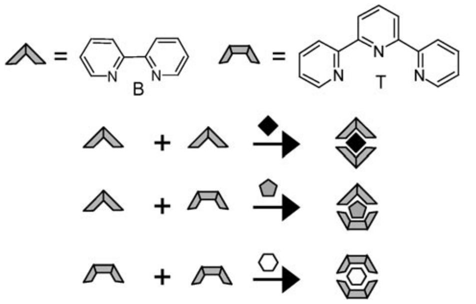

Figure 1. Coordination patterns and corresponding pair-coding with bidentate (B; bipyridine) and tridentate (T; terpyridine) ligand subunits; tetra- (e.g., $\mathrm{Cu^{I}}$), penta- (e.g., $\mathrm{Cu^{II}}$), and hexacoordinating (e.g., $\mathrm{Zn^{II}}$, $\mathrm{Fe^{II}}$) metal ions are represented for simplicity by a square, a pentagon and a hexagon, respectively.

Coordination subunits of various structures have been implemented for the generation of helicates,[4–8] our own work being based on the bidentate 2,2′-bipyridine (B) and on the tridentate 2,2′:6′2″-terpyridine (T) groups.[5–7,9a,12] Self-assembly modes of trinuclear double helicates have been represented schematically in Figure 1 of both references [3] and [12]. They formally involve pairing between the two B and T units through three patterns, tetra-, penta- or hexacoordination, akin to the pairing between the nucleobases A, G, T, and C through two interaction patterns, that is, two A=T or three G≡C hydrogen bonds, in the nucleic acid double helix. A pair of units, a "base pair", provides a code for metal-ion recognition; that is, B·B, T·T, and B·T coding for metal ions with tetra-, hexa-, and pentacoordination, respectively. A sequence of B and T units represents a codon, corresponding to an identical anticodon when the pairing is through even coordination (tetra, hexa) or to a complementary anticodon for odd coordination (penta). The two cases amount to operations of duplication (copying B into B, T into T) or translation (B into T or conversely).

Specifically, pairing between B and T subunits and metal cations of tetrahedral (such as $\mathrm{Cu^{I}}$ or $\mathrm{Ag^{I}}$) or octahedral (such as $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, or $\mathrm{Zn^{II}}$) coordination geometry, leads to the formation of [$\mathrm{BBM^{tet}}$] and [$\mathrm{TTM^{oct}}$] coordination centers as well as [$\mathrm{BTCu^{II}}$] centers[6] with the $\mathrm{Cu^{II}}$ cation, which presents preferential (B,T) pentacoordination, although with limited robustness (see below). Thus, homotritopic ligands containing either B or T units, that is, BBB and TTT strands, form double helicates with $\mathrm{Cu^{I}}$[5] and $\mathrm{Fe^{II}}$,[12] respectively, while a mixture of BBB and TTT gives a heterostranded double helicate with $\mathrm{Cu^{II}}$ cations.[6] Crystallographic studies have provided characterization of species such as [$\mathrm{M^{I}_3(BBB)_2}$] (M = Cu, Ag),[5] [$\mathrm{Fe^{II}_3(TTT')_2}$],[12] and [$\mathrm{Cu^{II}_3(BBB)(TTT')}$].[6] In the last two cases, the notation TTT′ designates ligands in which the terpyridine units are linked by ethylene bridges.

Heterotritopic ligands, as represented by BTB and TBT strands, give rise to particularly interesting systems with respect to control of binding selectivity and formation of specific heterometallic helicates.[7] In [$\mathrm{Cu^{I}_2Fe^{II}(BTB)_2}$], $\mathrm{Cu^{I}}$ and $\mathrm{Fe^{II}}$ are localized in the terminal four-coordinate B·B sites and in the central six-coordinate site, respectively, while in [$\mathrm{Cu^{II}_3(BTB)(TBT)}$], the three $\mathrm{Cu^{II}}$ ions are bound to the quinquedentate T·B "base pair", as in the [$\mathrm{Cu^{II}_3(BBB)(TTT')}$] species mentioned above.[6]

The present work is concerned with an exploration of the validity of the pair-coding of a set of tritopic ligand strands

Abstract in French: *Les métallohélicates à double brin sont connus pour manifester des propriétés d'auto-reconnaissance codées à la fois par la géométrie des métaux impliqués et par la topicité des ligands. En combinant dans un même brin trimère des sous-unités tridentées (terpyridine, T) et/ou bidentées (bipyridine, B), on génère un ensemble de ligands s'appariant en double hélices pouvant être homo- ou hétéroassemblées, homo- ou hétérotopiques, selon les propriétés de coordination des métaux impliqués. Ainsi, les quatre ligands BBB, TTT, BBT et TBT forment avec les ions* $\mathrm{Cu^{I}}$, $\mathrm{Cu^{II}}$ *et* $\mathrm{Zn^{II}}$ *une bibliothèque dynamique de double hélicates, correspondant au codage correct entre les paires BB, BT et TT et les cations tétra-, penta- et hexacoordinés* $\mathrm{Cu^{I}}$, $\mathrm{Cu^{II}}$ *et* $\mathrm{Zn^{II}}$ *respectivement.*

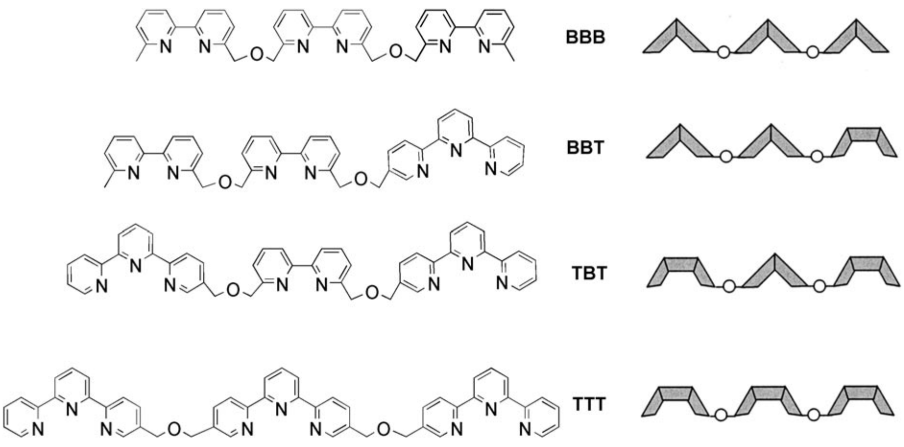

Figure 2. Left: The four tritopic ligand strands, based on a sequence of bipyridine and terpyridine coordination subunits, used in the present work for combined strand/metal ion recognition. Right: schematic representation of the ligand strands. The two spacers in TTT′ are -CH_2-CH_2- groups.

(Figure 2) for the metal ions Cu^I, Cu^{II}, and Zn^{II}. In an initial study,[7] in which Fe^{II} was used instead of Zn^{II}, the results were complicated apparently by the kinetic inertness of some of the Fe^{II} intermediates. The more labile Zn^{II} has proven preferable, as it provides systems that equilibrate more rapidly and in which the speciation is simpler. The fact that overall the behavior of Zn^{II} and Fe^{II} is similar points to the generality of the coding, as it is the type of coordination not the nature of the cation that determines the outcome.

Importantly, for the first transition-metal series, despite the fact that each metal exhibits various coordination numbers and geometries (even in a single oxidation state) in a broad range of complexes, polypyridine ligand units appear to evoke quite strong individual preferences for tetra-, penta-, or hexacoordination.

In conducting the present study of the species distribution arising when various mixtures of four tritopic polypyridine ligands (Figure 2) were added to solutions containing different mixtures of Zn^{II}, Cu^{II}, and Cu^I cations, it was anticipated that these would be labile systems, representing dynamic combinatorial libraries[10] distributed in accord with thermodynamic preferences, resulting (in part) from the nature of the coordination environments. Our aim was thus to establish in a complex system of constitutionally dynamic[11] metallosupramolecular species, that is, the double helicates, and the occurrence of information-directed self-assembly by self-selection of the correct double strand/metal cation partners from an equilibrating set of polytopic strands and metal cations. Electrospray mass spectrometry (ES-MS) was used as the primary tool for this work, its utility having been established earlier in a study of the self-assembly of pentanuclear double helicates.[13] However, it is clear that this method, while allowing the identification of the species present, does not give accurate quantitative information.

Results and Discussion

To obtain reference data, ES-MS studies were first performed on the species formed from the three cations Cu^I, Cu^{II}, and Zn^{II} and the monotopic B and T (bi- and ter-pyridine) ligands. In a mixture 2B, 2T, 1 Cu^I, and 1 Zn^{II}, only B-Cu^I-B and T-Zn^{II}-T species were formed, while a mixture of B, T, and Cu^{II} gave both pentacoordinate B-Cu^{II}-T and hexacoordinate T-Cu^{II}-T complexes together with remaining ligand B. A mixture of 2B, 2T, 1 Cu^{II}, and 1 Zn^{II} gave predominantly B-Cu^{II}-T and T-Zn^{II}-T species.

Given its preference for hexacoordination similar to that of Fe^{II} (results not shown), Zn^{II} may be considered as not only interesting in its own right, but also as a convenient model for what may be expected with Fe^{II} under forcing conditions to activate inert intermediates. Evidently, subtle differences between these two metal ions must arise and might well prove useful in exploring such factors as the difference between inner and outer sites of homostranded double helicates, differences that have been quantified in triple-helix systems.[8a]

The four tritopic ligands employed (Figure 2) all involved linkage of the B or T sites by 2-oxapropyl bridges; that is, BBB,[14] BBT,[7] TBT[7] and TTT (see Experimental Section). Assuming the codings $B \cdot B = Cu^I$, $B \cdot T = Cu^{II}$ and $T \cdot T = Zn^{II}$ to be valid, a mixture of all four ligands could give rise to a total of 11 different double-helical complexes in the presence of a mixture of the three cations Cu^I, Cu^{II}, and Zn^{II} (Figure 3).

Of these species, only $[Cu^I_3(BBB)_2]^{3+}$ has been structurally characterized as a double helicate, though both an analogue of **8**, $[Cu^{II}_3(TTT')(BBB)]^{6+}$ (**8′**)[6] and the Fe^{II} analogue of **5**, $[Fe^{II}_3(TTT')_2]^{6+}$ [12] have been similarly authenticated. Whether both helicate and nonhelicate species might

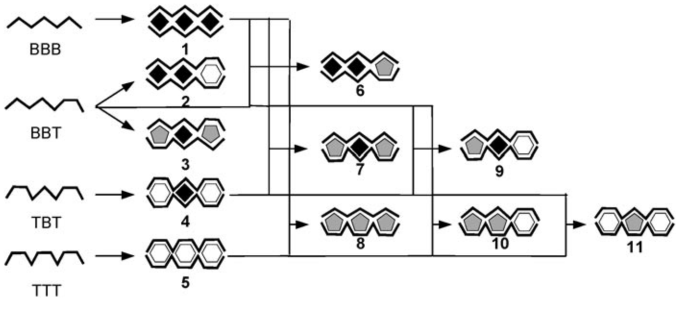

Figure 3. The 11 possible trinuclear complexes that may be formed with the four tritopic ligands BBB, BBT, TBT, and TTT (Figure 2) and a set of metal ions of tetra-, penta- and hexacoordination algorithms.

be present in solution mixtures is a matter requiring investigation by systematic characterization of the products from particular mixtures. In the present systems involving paramagnetic Cu^{II}, such analysis was heavily dependent on the use of ES-MS, which establishes composition but not spatial structure. Thus, ^1H NMR spectroscopy was an indispensable accompaniment for all diamagnetic species (involving only Cu^{I} and Zn^{II}). It is of interest to note, however, that although trinuclear species of heterostrand composition were found in the present work to give ES-MS peaks for several ion associates (with $[BF_4]^-$), in no case did they provide intense solvate peaks, a characteristic resulting probably from the absence in the helicate species of molecular cavities or clefts that might provide sites for holding solvent molecules.

It was expected that the nature of the species present in any mixture of the selected ligands and metal ions would depend not only on the ratios of reactants, but also on their concentrations and thus the concentration chosen for the present measurements was set at $\sim 10^{-4}\,mol\,L^{-1}$, a value known in the well-characterized BBB/Cu^{I} system to lead to the double helicate $[Cu^{I}_3(BBB)_2]^{3+}$, in which $>90\,\%$ of the total amount of metal is complexed.[5d] The overall results of ES-MS measurements showed that, for all systems investigated, this choice led to the prominence of bis(ligand)–trimetal species (associated with various numbers of counterions), indicating that while no doubt the stability constants for all species are not the same, all are of a value at least comparable to that of $[Cu^{I}_3(BBB)_2]^{3+}$. Care was also taken to achieve experimental conditions leading to thermodynamic equilibrium in the solvent used. To validate any ligand coding, it is not essential that the particular complex of interest be the sole or even the dominant species present, but that it should have the correct composition, be readily detectable, and that extensive coding errors be absent.

Generation of double helicates from single ligand strands

Strand BBB: Considering first the addition of the separate ligands to $Cu^{I}/Cu^{II}/Zn^{II}$ mixtures, the behavior of BBB in strongly favoring exclusive binding of Cu^{I} is well established,[5] so only the ES-MS of a solution containing BBB and Cu^{I} was investigated here. The most intense peak in the spectrum is that assigned to $[Cu^{I}_3(BBB)_2]^{3+}$ (*m/z* 451), with a much less intense peak corresponding to the ion-pair $\{[Cu^{I}_3(BBB)_2]\cdot BF_4\}^{2+}$ (*m/z* 719). The isotopical simulation of the ES-MS spectrum of the signal of triply charged $[Cu^{I}_3(BBB)_2]^{3+}$ is in perfect agreement with the experimental spectrum, thus allowing a unambiguous identification of the peak (See Supporting Information, Figure S1c,d). Interestingly, a peak of intermediate intensity corresponds to the species $[Cu^{I}(BBB)]^+$ (*m/z* 643), for which it is possible that the ligand is not in its extended form but instead is folded back and has wrapped itself about Cu^{I} to give tetrahedral coordination by binding with the first and second or the first and third bipyridine units. This species is not observed at high concentrations (10^{-2} M). Molecular modeling indicates that such entities can indeed form, but generally the ES-MS results support the indications from ^1H NMR and electronic absorption spectroscopic studies that the BBB/Cu^{I} system is rather simple.

Strand BBT: The case of the ligand BBT is special, since its symmetry is such that two double helicate forms, involving parallel (**2**) and antiparallel ligand strands (**3**) (Figure 3), are possible and are associated with different base-pairings.

Consistent with the coding anticipated for a parallel (head-to-head) arrangement, the electrospray mass spectrum for a mixture of BBT with one molar equivalent of Cu^{I} and half that amount of Zn^{II} shows a major peak for a bis(ligand) species with the composition $[Cu^{I}_2Zn^{II}(BBT)_2]^{4+}$ (**2**). Direct synthesis of this diamagnetic material and recording of its ^1H NMR spectrum revealed the diastereotopicity of the methylene protons expected for a helical (or a mesocate) structure.[4c] Further, COSY experiments enabled the complete assignment of all 30 inequivalent proton signals (aromatic and methylene) expected for C_2 symmetry, while ROESY measurements (See Supporting Information, Figure S2) showed the close proximity of the terminal B units of the two strands, reflected in the approach of the methyl group of one strand to the methylene group close to the terminal pyridine of the other strand, as anticipated from the structure of $[Cu^{I}_3(BBB)_2]$ (Figure 4). Furthermore, the ROESY spectrum provided no evidence for proximity of protons associated with B and T units of separate strands.

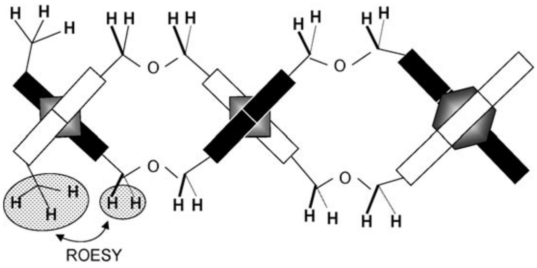

Figure 4. Proximity of the protons of the terminal CH_3 group of one BBT strand to the methylene protons on the second strand in the parallel-stranded double helicate $[Cu^{I}_2Zn^{II}(BBT)_2]^{4+}$ (**2**).

Addition of BBT to a 2:1 mixture of Cu^{II} and Cu^{I} also provided a solution for which most of the principal peaks in the high-resolution electrospray mass spectrum could be assigned to a single bis(ligand) species, containing three Cu ions and with an overall charge of 5+, associated with various numbers of either $[BF_4]^-$ or F^- ions. Thus, both isotopic peak separations and patterns were consistent with a peak at *m/z* 295 being due to $[Cu^{II}_2Cu^{I}(BBT)_2]^{5+}$, at *m/z* 374 to $\{[Cu^{II}_2Cu^{I}(BBT)_2]\cdot F^-\}^{4+}$, at *m/z* 391 to $\{[Cu^{II}_2Cu^{I}(BBT)_2]\cdot[BF_4]^-\}^{4+}$, at *m/z* 550 to $\{[Cu^{II}_2Cu^{I}(BBT)_2]\cdot[BF_4]^-)_2\}^{3+}$, at *m/z* 869 to $\{[Cu^{II}_2Cu^{I}(BBT)_2]\cdot([BF_4]^-)_3\}^{2+}$, and at *m/z* 1826 to $\{[Cu^{II}_2Cu^{I}(BBT)_2]\cdot([BF_4]^-)_4\}^{+}$. These data are consistent with the formation of the antiparallel (head-to-tail; **3**) double helicate species $[Cu^{II}Cu^{I}Cu^{II}(BBT)(TBB)]^{5+}$, expected for the coding that this array of B, T pairs implies. Although the paramagnetism of **3** excludes the use of ^{1}H NMR spectroscopy to establish its symmetry, it seems reasonable to assume a double-helical form given that this has been established crystallographically for both $[Cu^I_3(BBB)_2]^{3+}$[5a] and $[Cu^{II}_3(BBB)(TTT')]^{6+}$.[12] (Note that the presence of the fluoride ion in the *m/z* 374 species indicates that some degree of hydrolysis of BF_4^- may have occurred in solution.)

The formation of parallel- or antiparallel-stranded double helicates from the same pair of ligands and different sets of metal ions corresponds to a double expression of molecular information: processing the *same* molecular information by means of two different coordination algorithms (sets of metal ions) generates two different output species in a single-code/two-product fashion.[3]

Strands TBT and TTT: For the symmetrical ligands TBT and TTT, previous investigations[7] of their individual interactions with Cu^I/Fe^{II} mixtures have demonstrated the formation of species analogous to **4** and **5**, again consistent with the coding implicit in the helical bis(ligand) array. In the case of the analogue of **4**, the electrospray mass spectrum showed the predominance of a 1:1 Fe^{II}/TBT species, perhaps as a consequence of the ligand folding to envelop the cation and of the expected kinetic inertness of this helicate precursor. Replacement of Fe^{II} by Zn^{II} appears in all cases to result in rapid equilibration, with $TBT + Zn^{II} + 0.5\,Cu^I$ giving predominantly **4** and $TTT + 1.5\,Zn^{II}$ giving **5**. Considering the known structure of the Fe^{II} analogue of **5**,[12] it is assumed that the Zn^{II} complex is also double-helical. The ES-MS signal of the sixfold charged $[Zn^{II}(TTT)_2]^{6+}$ is in excellent agreement with the isotopical simulation (See Supporting Information, Figure S1 a,b).

Strand/cation self-selection in the assembly of double helicates from mixtures of ligands and metal ions: The goal of this work was to analyze the occurrence of complex reciprocal self-selection between ligand strands and metal cations as a function of the coordination subunits of the ligands and the coordination number of the ions.

1) For the various *binary mixtures* possible with the present ligands, it is expected that any (heteroligand) double-helical array would involve at least one site for Cu^{II} (Figure 3) and indeed combination of the different ligand pairs with the appropriate mixtures of metal ions led, in all cases, to the predominance of the species **6**–**11** in the electrospray mass spectra. The presence of the paramagnetic Cu^{II} center renders the ES-MS technique of particular importance in these instances. Noting that there are two isobaric pairs **3** and **7** within the full range of complexes possible, some ambiguities may be anticipated in the analysis of systems based on mixtures of more than two ligands (see below). Even with binary ligand mixtures and suitable choice of the nature and composition of the metal-ion mixture, various complications must be considered, the most evident being that both homo- and heteroligand-pairs may be present in any given double-helical species. For a precisely controlled metal ion composition and with specificity of binding, these are not necessarily of equal likelihood (i.e. assuming the metal ion composition controls the ligand pairing), but a 1:1 mixture of **1** and **3**, for example, would have the same overall composition as **6**. Indeed, a 1:1 mixture of BBB and BBT with $2\,Cu^I + Cu^{II}$ provides a mass spectrum showing significant peaks for all three species **1**, **3**, and **6**, all three corresponding to correct (2 strand + 3 cation) combinations. Entropic factors may favor the mixed-ligand species **6**, though they do not seem to be dominant, since the mixture generated from a solution of $BBB + TBT + Cu^I + 2\,Cu^{II}$ contains in addition to **7** as the major species, also detectable amounts of **1**.

Evidence that satisfaction of the local metal-ion requirements is the major factor influencing the helicate composition, that is, that the strength of the binding of a given metal ion to a given site (the "local" information) is not markedly dependent upon the nature of the adjoining sites, is provided in the system BBT + TBT, which is unique in that it may provide a ligand pair able to bind all three metal cations considered to give **9**. An equimolar mixture of BBT and TBT provides the three pairing combinations (BBT, TBT), $(TBT)_2$ and $(BBT)_2$ in which the strands may be either parallel or antiparallel. Treatment with an equimolar mixture $Cu^I + Cu^{II} + Zn^{II}$ yields indeed a mixture of helicates giving a mass spectrum dominated by the peaks corresponding to all four "correct" species **2**, **3**, **4**, and **9** (Figure 5).

2) Similarly, in progressing to a *ternary ligand mixture* but restricting the choice of metal ions to Cu^I and Zn^{II}, only the homoligand species **1**, **2**, and **5** are seen to be present in the product mixture, consistent with the fact that the coding in a heteroligand pair would require the presence of Cu^{II} for binding (Figure 3).

3) Proceeding further to a *quaternary ligand mixture* (BBB + BBT + TBT + TTT) and adding all three metal ions, the mass spectrum displays peaks due only to trimetallic–bis(ligand) species (given isobaric overlaps) incorporating

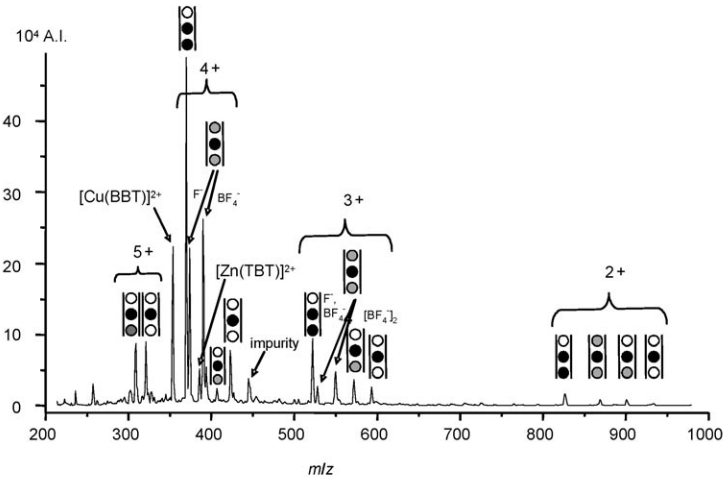

Figure 5. ES/MS spectrum of a mixture of $BBT + TBT + Cu^I + Cu^{II} + Zn^{II}$ showing the formation of all four possible double helicates corresponding to the correct (2 subunits/1 cation) combinations: **2**, **3**, **4** and **9**.

the correct selection of ligands and metal cations corresponding to the "base pair" coding provided by each pair of ligand strands (Supporting information, Figure S3).

Five-point reading—pentacoordination and the special case of Cu^{II}: Five coordination is required for the generation of heterotopic coordination centers from a combination of a bidentate and a tridentate coordination subunit. Similarly, heterostranded double helicates as well as translation, by B/T correspondence, also result from pentacoordination. Although there are some other cases of pentacoordination with other metal ions and binding units, Cu^{II} appears to occupy a unique place, by being the metal cation among all of them that fits best the requirements for the present purposes. As has been seen from experiments with the monotopic ligands B and T, Cu^{II} forms both B·T and T·T pairs so that (B,T) instructions and their reading by Cu^{II} appear to be less "robust" than are (B,B) and (T,T) four-point and six-point interactions with tetrahedrally and octahedrally coordinating cations, respectively. With the present tritopic ligands, the preferential coding of a B·T site for Cu^{II} appears to be obeyed, except in the particular case of BBB/TTT mixtures, for which species **8** ($[Cu_3(BBB)(TTT)]^{6+}$) is not detected in competition with $[Cu_3(TTT)_2]^{6+}$ (See Supporting Information, Figure S4). This contrasts markedly with the BBB/TTT′ system (the TTT′ ligand having ethylene rather than oxapropylene bridges), in which the ES-MS spectrum exhibits predominantly signals due to anion associates of $[Cu^{II}_3(BBB)(TTT')]^{6+}$ (See Supporting information, Figure S5), the structure of which has also been confirmed in the solid state by X-ray crystallography.[6] Thus, in any heterostrand species, a common bridge between donor units is not necessarily ideal.

In addition to the consequences of the choice of the B and T subunits, the detailed structure of the strands appears to play an important role, in particularly their commensurability and flexibility. As already pointed out, the Cu^{II} coordination instructions are not fully "robust" with respect to coordination number five or six. Furthermore, a pentacoordinate BT·Cu^{II} center may be have either trigonal bipyramidal or square pyramidal geometry. In the crystal structure, BT·Cu^{II} has a square pyramidal geometry[15a,b] and in the $[Cu^{II}_3(BBB)(TTT')]$ double helicate, the terminal centers are square pyramidal, whereas the central one is trigonal bipyramidal.[6,15c] Assuming that binding of the tridentate units would be energetically dominant, it may be that it is the array of bidentate sites that must accommodate most to any mismatch. Hence, if the oxapropylene bridges of BBB cannot adapt sufficiently to match the requirements of a $[Cu^{II}_3(TTT)]^{6+}$ unit, this might lead to the relative destabilization of $[Cu_3(BBB)(TTT)]^{6+}$. Shortening the links between tridentate units, as in TTT′, would make the ligand commensurable with the BBB strand, which could explain the return to favoring of pentacoordination, as in $[Cu_3(BBB)(TTT')]^{6+}$. On the other hand, bridge matching in $[Cu_3(BBB')(TTT')]^{6+}$ also leads to the dominance of the heterostrand species. As in all systems involving thermodynamic equilibria between multiple species, this may either result from an intrinsic stability of a given species, here $[Cu^{II}_3(BBB')(TTT')]$, or to an intrinsic destabilization of another member of the equilibrating system, that is, $[Cu^{II}_3(TTT')]$, due to the lack of flexibility of the ethylene bridges.

Other factors, such as differences in rotational energy within the bridges or in stacking interactions between the aromatic units of the ligands, must play a part. Although one may wish to explore other [(metal ion)$^{n+}$(bidentate site)(tridentate site)] combinations, the [Cu^{II}, B, T] unit, despite limited robustness, nevertheless offers good information-processing capability,[16] as illustrated by the role it plays in multinuclear systems presenting multiple expression of molecular information[17] and dominant/recessive behavior.[18]

Conclusions

While it has not been shown that in every case studied here the trimetallic–bis(ligand) species detected by ES-MS has a double helical structure, this is a plausible rationalization of all the present results, consistent with both the spectroscopic and crystallographic observations for several species.

If, as in the present work, the binding of all metal ions involved is labile, it becomes possible to rapidly establish equilibrium mixtures of (double) helicate complexes involving poly(B/T) ligands in which the particular strand pairings are determined by specific coordination preferences of the cations. Provision of the appropriate metal-ion mixture may thus be used to control ligand pairing by means of the information contained in the mixture of metal ions and ligands.[19] Clearly, complications may arise when a broader range of metal ions than Cu^{I}, Cu^{II}, and Zn^{II} is considered. Also, the differences between Cu^{I} and Cu^{II} indicate that there may be many useful subtleties to be explored in the use of redox-active transition-metal ions to control ligand assembly, as is the case in the electrochemical interconversion between two highly intertwined multinuclear architectures[17] or between two states of a catenate.[20]

One of the remarkable features of helicate ligand binding is the occurrence of "self-recognition", meaning that for a mixture of strands of differing topicity, addition of a metal ion compatible with helicate formation results preferentially in the pairing of ligands of the same topicity.[9a] This suggests the possibility of devising an analogue of the polymerase chain reaction[21] in which coordination subunits, functionalized so as to enable their reversible linkage (for instance, through imine groups[9d]), would first be assembled on a primer strand under the control of metal-ion coordination "base-pair" coding; the newly assembled strand would thereafter be irreversibly connected by post-assembly modification (e.g. reduction of imine groups), and finally strand separation by sequestering the metal ions would prepare the stage for the next round.[22] Given the observed effect of differences in the linking units between donor sites on the stability of mixed-ligand species, an appealing prospect would be that the linking reaction might automatically lead to the ejection of the newly generated ligand.

To read the message considered to be conveyed by the formation of a given helicate, it must, of course, be possible to detect that helicate. This does not mean that it must be the only assembly present on the supramolecular "page", but simply that it must be spatially, energetically, or temporally separable from the other species present (which may themselves carry other messages, perhaps more inscrutable). In the systems currently described, not only are the species [MM′M″LL′] readily isolated and detected by ES-MS, but they are generally major components of the reaction mixtures. Of much interest in the perspective of the present work is the exploration of coordination units other than B and T and of their ability to undergo complementary pairing with metal cations. Triple-stranded helicates might be considered, based for instance on the combination of B and T with strands containing monodentate pyridine groups.

One of the prospects for the use of ligands described herein is in the construction of a more sophisticated analytical dictionary so as to be able to decipher the information contained in the ligand/metal-ion coordinative language. In the conventional analytical technique of inductively coupled plasma mass spectrometry (ICP-MS), for example, a single signal (ion current) identifies a single element. For ES-MS of solutions containing polytopic ligands, a single signal may identify several elements (as a particular mixture), depending upon the ligand topicity. There is still much work to be done, however, to establish ways of converting the qualitative information of the nature of the species present into the quantitative information of how much there is of each.

In summary, the present systems involving mixtures of several ligand strands and metal ions have enabled conduct of a dynamic exploration of the supramolecular constitutional space[11] under the control of the processing of molecular information, driven by recognition between complementary coordination subunit/metal-cation pairing involving specific interactional algorithms,[3] and resulting in a process of self-organization by selection[11] of the correct components.

Experimental Section

Materials and general methods: The following compounds were prepared as previously described: BBB,[14] BBT,[7] TBT.[7] The following reagents were purchased from commercial sources: Cu^{II}[BF$_4$]$_2$ (Aldrich), Zn^{II}[BF$_4$]$_2$ (Aldrich). 400 MHz ^{1}H NMR spectra were recorded on a Bruker Ultrashield Avance 400 spectrometer. The solvent residual signal[23] was used as an internal reference for ^{1}H NMR spectra. The following notation is used for the ^{1}H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m). The two-dimensional NMR experiments used were: COSY (correlation spectroscopy), NOESY (nuclear Overhauser enhancement spectroscopy or nuclear Overhauser and exchange spectroscopy), ROESY (rotating-frame Overhauser enhancement (effect) spectroscopy); they were done on 500 MHz Bruker spectrometers. FAB-MS, EI-MS, and ES-MS measurements were performed by the Service de Spectrométrie de Masse, Université Louis Pasteur. Melting points were recorded on a Büchi Melting Point B-540 apparatus and are uncorrected.

Spectrometric analysis of the helicate mixtures

Mass spectrometry: Spectra for the solution equilibrium studies were obtained using electrospray ionization on three different instruments, considerable time being devoted to establishing the optimum conditions for detection of the helicates on each. Signal attributions were verified by comparing the high-resolution ES-MS data to isotopical simulations. Metal and ligand mixtures were prepared from stock solutions of the separate ligands and the metal salts Cu^{I}BF$_4$, Cu^{II}[BF$_4$]$_2$, and Zn^{II}[BF$_4$]$_2$ in acetonitrile. The solutions finally injected into the spectrometers were diluted so that the total ligand concentration was 10^{-4} M.

Calibration: (for all) Calibration was performed using the multiply charged peaks of protonated horse heart myoglobin (2 μM, in water/acetonitrile 50/50 (v/v) acidified with 1% HCOOH. For calibration in the high-resolution mode, the singly charged clusters of $[(H_3PO_4)_nH^+]^+$ ($n=2$–20) were used by injecting a solution of 0.01% H$_3$PO$_4$ in water/acetonitrile 50/50 (v/v).

MicroTof: High-Resolution ESI mass spectra in positive mode were acquired on a time-of-flight mass spectrometer (microTof, Bruker Daltonics, Bremen, Germany). The ESI-source was heated to 200°C. Sample solutions were introduced into the mass spectrometer source with a syringe pump (Cole Parmer, Vernon Hills, Illinois, USA) with a flow rate of 3 μL min^{-1}. Scanning was performed on an m/z range from 50–3000, data was averaged for 1 min and then smoothed using the Gaussian algorithm.

Quattro II: ESI mass spectra in positive mode were acquired on a triple quadrupole mass spectrometer (Quattro II, Micromass, Altrincham, UK) in the positive mode. The ESI-source was heated to 80°C. Sample solutions were introduced into the mass spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, USA) with a flow rate of 3 μL min^{-1}. Scanning was performed on an m/z range from 200–3000 in 28 s; five scans were summed to obtain the final spectrum.

MSD: To get comparative results, selected mixtures were also analyzed with a second quadrupole mass spectrometer (Mass Selective Detector, Series 1100 MSD, Hewlett Packard Inc, Toronto, Canada) in the positive mode. The desolvation gas temperature was set to 300°C, sample solutions were introduced into the mass spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, USA) with a flow rate of 3 μL min^{-1}. Scanning was performed on an m/z range from 200–1200 in 10 seconds; five scans were summed to obtain the final spectrum. Spectra were smoothed using the Gaussian algorithm.

Synthesis: Syntheses of functionalized bipyridine units and tritopic ligands derived from them were described previously,[14] as were those of ligands closely related to those used that contained terpyridine units.[7,10] Hence, only a selection is presented herein as illustrative of the general synthetic procedures.

5-Bromomethyl-2,2′-6′,2″-terpyridine:[12] In rapid succession, *N*-bromosuccinimide (1.07 g, 6 mmol) and benzoylperoxide (0.23 g, 0.33 mmol) were added to a solution of 5,5″-dimethyl-2,2′-6′,2″-terpyridine (1 g, 4 mmol) in CCl$_4$ (100 mL). The resulting yellow solution was heated under Ar at 95°C for 55 min before being filtered while hot, and the solvent removed in vacuo. Purification was achieved by column chromatography (silica; CH$_2$Cl$_2$) and by recrystallization from CHCl$_3$/hexane (0.891 g, 68% yield). M.p. 224–225°C; ^{1}H NMR (200 MHz; CDCl$_3$): $\delta=8.69$ (m, 2H; H6, H6″), 8.60 (br d, $J=7.8$ Hz, 2H; H3, H3″), 8.46 (dd, $J=7.8$, 0.9 Hz, 1H; H3′), 8.44 (dd, $J=7.8$, 0.9 Hz, 1H; H5′), 7.96 (t, $J=7.8$ Hz, 1H; H4′), 7.86 (m, 2H; H4, H4″), 7.33 (ddd, $J=7.5$, 4.8, 1.2 Hz, 1H; H5″), 4.56 ppm (s, 2H; CH$_2$Br); MS (EI): m/z (%): 327 (6) $[M+Br^{81}]^+$, 325 (6) $[M+Br^{79}]^+$, 247 (38), 246 (100) $[M-Br]^+$. Polybrominated products could be reduced to monobrominated products by the use of DIBAL (DIBAL = diisobutylaluminum hydride) in CH$_2$Cl$_2$ at −78°C.

5,5″-Bis(bromomethyl)-2,2′-6′,2″-terpyridine:[12] In rapid succession, *N*-bromosuccinimide (5.55 g, 31.19 mmol) and benzoylperoxide (0.23 g, 0.94 mmol) were added to a solution of 5,5″-dimethyl-2,2′-6′,2″-terpyridine (1.63 g, 6.24 mmol) in CCl$_4$ (150 mL). The resulting yellow solution was heated under Ar at 95°C for 55 min before being filtered while hot. Insoluble material present was washed with CCl$_4$ (2×75 mL), the washings combined with the initial filtrate, and the total evaporated under vacuum to give a yellow paste. This paste was dissolved in CH_2Cl_2 (300 mL) and washed with aqueous $Na_2S_2O_3$ (0.5 M; 3×100 mL). The combined aqueous washings were back-extracted with CH_2Cl_2 (100 mL), and the combined organic phases were then dried over Na_2SO_4 before the solvent was removed in vacuo. The yellow residue obtained was recrystallized twice from CCl_4 to obtain pure 5,5″-bis(bromomethyl)-2,2′-6′,2″-terpyridine (0.27 g; 10 %). Considerable additional material was subsequently obtained by reduction of higher bromination products with DIBAL. Thus, the CCl_4-soluble material was recovered by evaporation of the solvent, then dissolved in CH_2Cl_2 (120 mL) and cooled to −78 °C. DIBAL (1 M in CH_2Cl_2) was added until TLC indicated that only dibromide was present, the solution then being green. Saturated aqueous NH_4Cl (70 mL) was added and the mixture allowed warm to room temperature. Water (150 mL) was added and the mixture filtered through Celite, the filter pad being subsequently washed with CH_2Cl_2. The total organic phase was washed with water (2×150 mL), dried over Na_2SO_4 and the solvent removed in vacuo. Recrystallization of the residue from CH_2Cl_2 provided more product as a very pale yellow powder (1.20 g; 46 % yield). M.p. 189–191 °C; ^{1}H NMR (200 MHz; $CDCl_3$): $\delta=8.72$ (d, $J=2.2$ Hz, 2H; H6, H6″), 8.61 (d, $J=8.1$ Hz, 2H; H3, H3″), 8.47 (d, $J=7.8$ Hz, 2H; H3′, H5′), 7.97 (t, $J=7.8$ Hz, 1H; H4′), 7.91 (dd, $J=8.1$, 2.2 Hz, 2H; H4,H4″), 4.57 ppm (s, 4H; 2 CH_2Br); MS (EI): m/z (%): 419.9 (100), $[M+H]^+$ with expected isotopic pattern), 391 (49), 340/338 (22/22) $[M-Br]^+$.

5-Acetoxymethyl-2,2′-6′,2″-terpyridine: CH_3CO_2Na (3.92 g, 48 mmol) was added to a solution of 5,5″-bis(bromomethyl)-2,2′-6′,2″-terpyridine (2.60 g, 8.0 mmol) in DMF (120 mL) and the mixture heated at 140 °C for 20 h. The organic fractions were dried over Na_2SO_3 and the solvent removed in vacuo to yield the methylacetate as a white solid (2.10 g, 86 % yield) sufficiently pure for direct use in the next step. ^{1}H NMR (200 MHz; $CDCl_3$): $\delta=8.65$ (br s, 2H; Ar), 8.56 (br d, $J=8.0$ Hz, 2H; Ar), 8.40 (br d, $J=7.7$ Hz, 2H; Ar), 7.96–7.77 (m, 3H; Ar), 7.96–7.77 (m, 3H; Ar), 7.32–7.25 (m, 1H; Ar), 5.16 (s, 2H; CH_2OAc), 2.09 ppm (s, 3H; -O_2CH_3).

5,5″-Bis(acetoxymethyl)-2,2′-6′,2″-terpyridine: CH_3CO_2Na (2.12 g) was added to a solution of 5,5″-bis(bromomethyl)-2,2′-6′,2″-terpyridine (0.90 g) in DMF (40 mL) and the mixture was heated, under Ar, at 140 °C for 19 h. Removal of the solvent in vacuo gave a pale brown solid, which was extracted with $CHCl_3$ and filtered through Celite to remove NaBr. Evaporation of the solvent provided material (0.80 g, 99 % yield) sufficiently pure for direct use in the next step.

5-Hydroxymethyl-2,2′-6′,2″-terpyridine: Solutions of 5-acetoxymethyl-2,2′-6′,2″-terpyridine (1.435 g, 4.7 mmol) in CH_3OH (100 mL) and NaOH (1.20 g) in water (20 mL) were mixed and heated at reflux for 17 h. On cooling, the solution was concentrated in vacuo and then diluted with water (90 mL). The product, which formed a suspension, was extracted into CH_2Cl_2 until no terpyridine could be detected in the aqueous phase. The combined extracts were dried over Na_2SO_4 then evaporated to dryness, giving the product as a white crystalline solid (1.095 g, 82 % yield). M.p. 131 °C; ^{1}H NMR (200 MHz; $CDCl_3$): $\delta=8.65$–8.61 (m, 1H; Ar), 8.53–8.49 (m, 2H; Ar), 8.44 (d, $J=8.2$ Hz, 1H; Ar), 8.33 (d, $J=7.9$ Hz, 2H; Ar), 7.87 (t, $J=7.9$ Hz, 1H; Ar), 7.80 (td, $J=7.7$, 1.8 Hz, 1H; Ar), 7.73 (dd $J=8.1$, 2.1 Hz, 1H; Ar), 7.29 (ddd, $J=7.5$, 4.9, 1.2 Hz, 1H; Ar 5″), 4.69 (br s, 2H; CH_2OH), 3.86 ppm (br, 1H; OH); ^{13}C NMR (50.33 MHz; $CDCl_3$): $\delta=156.1$, 155.3, 155.1, 154.9 (Ar-C, *o*-N), 148.9, 147.7 (Ar-CH, *o*-N), 137.8, 136.9 (Ar-CH, *p*-N), 136.5 (Ar-CCH_2OH, *m*-N), 135.7 (Ar-CH, *p*-N), 123.7, 121.3, 120.9 (Ar-CH, *m*-N), 62.3 ppm (CH_2OH); MS (EI): m/z (%): 264, 263 (19:100) $[M]^+$, 262 (35) $[M-H]^+$, 246 (20) $[M-OH]^+$, 234 (57) $[M-CHO]^+$, 149 (36), 78 (38).

5,5″-Bis(hydroxymethyl)-2,2′-6′,2″-terpyridine: Solutions of 5,5″-bis(acetoxymethyl)-2,2′-6′,2″-terpyridine (0.81 g) in CH_3OH (50 mL) and NaOH (1.20 g) in water (20 mL) were mixed and heated at reflux for 17 h. On cooling, the solution was concentrated in vacuo and then diluted with water (50 mL). The product, which formed a suspension, was extracted into $CHCl_3$ (50 mL), the extractions being repeated until no terpyridine could be detected in the aqueous phase. The combined extracts were dried over Na_2SO_4 then evaporated to dryness, giving the product as a white crystalline solid (0.50 g, 80 % yield). M.p. 154–156 °C; ^{1}H NMR (200 MHz; CD_3OD): $\delta=8.59$ (d, $J=1.7$ Hz, 2H; H6, H6″), 8.50 (d, $J=8.1$ Hz, 2H; H3, H3″), 8.27 (d, $J=7.8$ Hz, 2H; H3′,H5′), 7.93 (t, $J=7.8$ Hz, 1H; H4′), 7.89 (dd, $J=8.1$, 1.7 Hz, 2H; H4, H4″), 4.70 ppm (s, 4H; 2 CH_2OH); MS (EI): m/z (%): 293 (100) $[M]^+$, 292 (24) $[M-H]^+$, 276 (15) $[M-OH]^+$, 264 (52), 262 (11) $[M-CH_2OH]^+$.

Ligand strand TTT: Under Ar, KO*t*Bu (0.112 g, 1 mmol) was added to a solution of 5,5″-di(hydroxymethyl)-2,2′-6′,2″-terpyridine (0.147 g, 0.5 mmol) in THF (20 mL) turning the colorless solution to pale orange. The mixture was stirred for 1 h at room temperature before adding 5-bromomethyl-2,2′-6′,2″-terpyridine (0.326 g, 1 mmol) and stirring for 17 h. The precipitate was obtained upon filtration and washed with water, MeOH, and diethyl ether to give TTT as a white powder (0.288 g, 74 % yield). M.p. 199–201 °C; ^{1}H NMR (500 MHz; 10 % CF_3SO_3D in [D$_6$]acetone): $\delta=9.54$ (br s, 2H; Ar), 9.47 (br s, 2H; Ar), 9.37 (d, $J=6.0$ Hz, 2H; Ar), 9.15 (m, 6H; Ar), 9.04 (m, 6H; Ar), 8.91 (m, 6H; Ar), 8.61 (t, $J=7.9$ Hz, 2H; Ar), 8.61 (m, 1H; Ar), 8.43 (ddd, $J=7.4$, 6.0, 1.1 Hz, 2H; Ar), 5.30 ppm (s, 8H; 4 CH_2O); MS (FAB): m/z (%): 784 (31) $[M+H]^+$, 522 (10) $[M-\text{terpy}CH_2O]^+$, 345 (25), 262 (28) $[\text{terpy}CH_2O]^+$, 247 (33), 192 (100); HS-MS (MicroTOF): m/z: 784.31 $[M+H]^+$, 806.29 $[M+Na]^+$.

Ligand strand TBT: Following the same procedure as for the synthesis of TTT, 6,6′-di(hydroxymethyl)-2,2′-bipyridine (0.173 g, 0.8 mmol) and 5-bromomethyl-2,2′-6′,2″-terpyridine (0.522 g, 1.6 mmol) gave TBT as a white powder (0.311 g, 55 % yield). M.p. 196–198 °C; ^{1}H NMR (400 MHz; $CDCl_3$): $\delta=8.73$ (d, $J=2.0$ Hz, 2H; terpy H6″), 8.70 (br dd, $J=4.7$, 1.8 MHz, 2H; terpy H6), 8.63 (d, $J=8.1$ Hz, 2H; terpy H3″), 8.62 (br d, $J=7.7$ Hz, 2H; terpy H3), 8.46 (d, $J=8.0$ Hz, 4H; terpy H3′ H5′), 8.34 (d, $J=7.8$ Hz, 2H; bpy H5), 7.96 (t, $J=8.0$ Hz, 2H; terpy H4′), 7.92 (dd, $J=8.1$, 2.0 Hz, 2H; terpy H4″), 7.86 (td, $J=7.4$, 1.8 Hz, 2H; terpy H4), 7.85 (t, $J=7.8$ Hz, 2H; bpy H3), 7.53 (ddd, $J=7.4$, 4.7, 1.1 Hz, 2H; terpy H5), 4.84 (s, 4H; 2 CH_2O), 4.80 ppm (s, 4H; 2 CH_2O); ^{13}C NMR (50.33 MHz; $CDCl_3$): $\delta=157.7$, 156.3, 155.9, 155.6, 155.4, 155.2 (Ar-C, *o*-N), 149.2, 148.7 (Ar-CH, *o*-N), 137.9, 137.6, 136.9, 136.5 (Ar-CH, *p*-N), 133.6 (Ar-CCH_2O, *m*-N), 123.8, 121.5, 121.2, 121.0, 120.9, 120.0 (Ar-CH, *m*-N), 73.6 (CH_2), 70.3 ppm (CH_2); MS (FAB): m/z (%): 707 (75) $[M+H]^+$, 491 (43), 247 (100).

Ligand strand BBT: Following the same procedure as for the synthesis of TTT, 5-hydroxymethyl-2,2′-6′,2″-terpyridine (0.171 g, 0.65 mmol) and 6′-(bromomethyl)-6‴-methyl-6,6″-[oxybix(methylene)]bis(2,2′-bipyridine)[14] (0.300 g, 0.65 mmol) gave BBT as a white powder (0.251 g, 60 % yield). M.p. 206–208 °C; ^{1}H NMR (200 MHz; CDCl3): $\delta=8.72$ (m, 2H; Ar), 8.63 (m, 2H; Ar), 8.46 (d, $J=7.8$ Hz, 2H; Ar), 8.33 (m, 3H; Ar), 8.19 (d, $J=7.9$ Hz, 1H; Ar), 8.0–7.8 (m, 6H; Ar), 7.68 (t, $J=7.7$ Hz, 1H; Ar), 7.60–7.51 (m, 3H; Ar), 7.34 (ddd, $J=7.5$, 4.8, 1.2 Hz, 1H; terpy H5″), 7.16 (d $J=7.6$ Hz, 1H; Ar), 4.91 (s, 4H; 2 CH_2O), 4.83 (s, 4H; 2 CH_2O), 4.80 (s, 2H; CH_2O), 2.63 ppm (s, 3H; Me); MS (FAB): m/z (%): 646, 645, 644 (100:48:14) $[M+H]^+$, 455 (29), 383 (34), 262 (31) $[\text{terpy}CH_2O]^+$, 246 (50) $[\text{terpy}CH_2]^+$, 199 (73) $[\text{bpy}CH_2O]^+$, 184 (60), 165 (38); HS-MS (MicroTOF): m/z: 644.27 $[M+H]^+$, 666.25 $[M+Na]^+$.

Preparation of the complexes 1–11: Stock solution of the ligands BBB, BBT, TBT, and TTT in CH_2Cl_2 (10^{-2} M, 100 mL) and of $[Cu^I(CH_3CN)_4]BF_4$, $[Cu^{II}(CH_3CN)_4][BF_4]_2$, $Zn^{II}[BF_4]_2\cdot 8H_2O$ in CH_3CN (10^{-2} M, 100 mL) were prepared. The appropriate amounts of ligands strands and metallic cations were mixed, the resulting solution evaporated and redissolved in pure CH_3CN (0.500 mL) so that the concentration in complex would be 5.10^{-5} M, and injected in the spectrometer without any further purification.

Data for 1:[5a] ^{1}H NMR (400 MHz; CD_3CN): $\delta=8.29$ (d, $J=9$ Hz, 4H; Ar), 8.26 (d, $J=9$ Hz, 4H; Ar),8.26 (d, $J=9$ Hz, 4H; Ar), 8.17 (d, $J=9$ Hz, 4H; Ar), 8.08 (t, $J=9$ Hz, 4H; Ar), 7.98 (t, $J=9$ Hz, 4H; Ar), 7.75 (t, $J=9$ Hz,4H; Ar), 7.51 (d, $J=9$ Hz, 4H; Ar), 6.95 (d, $J=9$ Hz,4H; Ar), 6.77 (d, $J=9$ Hz, 4H; Ar), 3.87 (AB, $J=12$ Hz, 4H; CH_2O), 3.85 (AB, $J=12$ Hz, 4H; CH_2O), 3.68 (AB, $J=12$ Hz, 4H; CH_2O), 3.61 (AB, $J=12$ Hz, 4H; CH_2O), 2.16 ppm (s, 12H; CH_3); ES-MS: m/z calcd for $\{[Cu^I_3(BBB)_2][(BF_4)]\}^{2+}=[C_{72}H_{64}BCu_3F_4N_{12}O_4]^{2+}$: 719.40; found: 719.16; calcd for $[Cu^I_3(BBB)_2]^{3+}=[C_{72}H_{64}Cu_3N_{12}O_4]^{3+}$: 450.66; found: 450.47

(see Supporting information); additional peak: $[Cu^{I}(BBB)(BF_4)]$: calcd for $[Cu^{I}(BBB)]^{+}=[C_{36}H_{32}CuN_6O_2]^{+}$: 643.19; found: 643.19;

Data for 2: ^{1}H NMR (400 MHz; CD_3CN): $\delta=8.78$ (s, 6H; terpy H3′, H4′, H5′), 8.54 (d, *J*=6.4 Hz, 2H; terpy H3″), 8.53 (d, *J*=4.2 Hz, 2H; bpy H3‴), 8.41 (d, *J*=6.4 Hz, 2H; bpy H5″), 8.34 (d, *J*=8.4 Hz,2H; bpy H3), 8.32 (t, *J*=8 Hz,2H; bpy H4‴), 8.31 (d, *J*=(:! Hz, 2H; bpy H3′), 8.17 (d, *J*=6.5 Hz, 2H; terpy H3), 8.15 (t, *J*=6.3 Hz, 2H; bpy H4), 8.13 (t, *J*=6.3 Hz, 2H; terpy H4‴), 7.99 (t, *J*=6.4 Hz, 2H; bpy H4‴), 7.92 (t, *J*=6.4 Hz, 2H; bpy H4′), 7.74 (s, 2H; terpy H6), 7.56 (d, *J*=5.9 Hz, 4H; terpy H6‴, bpy H5), 7.42 (d, *J*=6 Hz, 2H; bpy H5‴), 7.37 (dd, *J*=4.2 Hz, 4.1 Hz, 2H; terpy H5‴), 7.30 (d, *J*=6.4 Hz, 2H; terpy H4), 6.99 (d, *J*=6 Hz, 2H; bpy H5′), 6.95 (d, *J*=6.2 Hz, 2H; bpy H5″), 4.49 (d, *J*=13.33 Hz, 2H; bpy-CH_2OC*H*H-tpy), 3.99 (d, *J*=13.63 Hz, 2H; bpy-C*H*HOCH_2-bpy), 3.95 (d, *J*=13.67 Hz, 2H; bpy-CH_2OC*H*H-bpy), 3.79 (d, *J*=13.30 Hz, 2H; bpy-CH_2OC*H*H-terpy), 3.76 (d, *J*=13.63 Hz, 4H; bpy-CH*H*OCH_2-bpy bpy-CH*H*OCH_2-terpy,), 3.66 (d, *J*=13.67 Hz, 2H; bpy-CH_2OCH*H*-bpy), 3.22 (d, *J*=13.63 Hz, 2H; bpy-CH*H*OCH_2-terpy), 2.18 ppm (s, 6H; CH_3-bpy); ES-MS: *m/z* calcd for $[(BBT)_2Cu^{I}_2Zn^{II}(BF_4)_2]^{2+}=[C_{80}H_{66}B_2Cu_2F_8N_{14}O_4Zn]^{2+}$: 826.78; found: 826.17; calcd for $[Cu^{I}_2Zn^{II}(BBT)_2(BF_4)]^{3+}=[C_{80}H_{66}BCu_2F_4N_{14}O_4Zn]^{3+}$: 522.25; found: 521.78; calcd for $[Cu^{I}_2Zn(BBT)_2]^{4+}=[C_{80}H_{66}Cu_2N_{14}O_4Zn]^{3+}$: 369.98; found: 369.60, 445.12.

Data for 3: ES-MS: *m/z* calcd for $[Cu^{II}_2Cu^{I}(BBT)_2(BF_4)_4]^{+}=[C_{80}H_{66}B_4Cu_3F_{16}N_{14}O_4]^{+}$: 1825.33; found: 1825.85; 1187.85; calcd for $[Cu^{II}_2Cu^{I}(BBT)_2(BF_4)_3]^{2+}=[C_{80}H_{66}B_3Cu_3F_{12}N_{14}O_4]^{2+}$: 868.17; found: 868.85; calcd for $[Cu^{II}_2Cu^{I}(BBT)_2(BF_4)_2]^{3+}=[C_{80}H_{66}B_2Cu_3F_8N_{14}O_4]^{3+}$: 550.51; found: 550.28, $[Cu^{II}_2Cu^{I}(BBT)_2(BF_4)]^{4+}=[C_{80}H_{66}BCu_3F_4N_{14}O_4]^{4+}$: 391.22; found: 391.07; calcd for $[Cu^{II}_2Cu(BBT)_2{}^{I}F]^{4+}=[C_{80}H_{66}Cu_3FN_{14}O_4]^{4+}$: 374.27; found: 374.08; calcd for $[Cu^{II}_2Cu^{I}(BBT)_2]^{5+}=[C_{80}H_{66}Cu_3N_{14}O_4]^{5+}$: 295.62; found: 295.38; additional peaks: $[Cu^{II}(BBT)][BF_4]_2$: calcd for $[Cu^{II}(BBT)]^{2+}=[C_{40}H_{33}CuN_7O_2]^{2+}$: 353.64; found: 353.45.

Data for 4: ES-MS: *m/z* calcd for $[Zn^{II}_2Cu^{I}(TBT)_2(BF_4)_3]^{2+}=[C_{88}H_{68}B_3CuF_{12}N_{16}O_4Zn_2]^{2+}$: 934.16; found: 933.66; calcd for $[Zn^{II}_2Cu^{I}(TBT)_2(BF_4)_2]^{3+}=[C_{88}H_{68}B_2CuF_8N_{16}O_4Zn_2]^{2+}$: 593.84; found: 593.25; calcd for $[Zn^{II}_2Cu^{I}(TBT)_2(BF_4)]^{4+}=[C_{88}H_{68}BCuF_4N_{16}O_4Zn_2]^{4+}$: 423.68; found: 423.44; calcd for $[Zn^{II}_2Cu^{I}(TBT)_2]^{5+}=[C_{88}H_{68}CuN_{16}O_4Zn_2]^{4+}$: 321.58; found: 321.33, 257.10 additional peaks: $[Zn^{II}(TBT)][BF_4]_2$: calcd for $[Zn^{II}(TBT)(BF_4)]^{+}=[C_{44}H_{34}BF_4N_8O_2Zn]^{+}$ 857.21; found: 857.21; calcd for $[Zn^{II}(TBT)]^{2+}=[C_{44}H_{34}N_8O_2Zn]^{2+}$ 385.10; found: 385.40; [454.0]

Data for 5: ES-MS: *m/z* calcd for $[Zn^{II}_3(TTT)_2(BF_4)_4]^{2+}=[C_{98}H_{74}B_4F_{16}N_{18}O_4Zn_3]^{2+}$: 1055.57; found: 1055.90; calcd for $[Zn^{II}_3(TTT)_2(BF_4)_3]^{3+}=[C_{98}H_{74}B_3F_{12}N_{18}O_4Zn_3]^{3+}$: 674.78; found: 674.60; calcd for $[Zn^{II}_3(TTT)_2(BF_4)_2]^{4+}=[C_{98}H_{74}B_2F_8N_{18}O_4Zn_3]^{4+}$: 484.38; found: 484.20; calcd for $[Zn^{II}_3((TTT)_2BF_4)]^{5+}=[C_{98}H_{74}BF_4N_{18}O_4Zn_3]^{5+}$: 370.14; found: 369.88; calcd for $[Zn^{II}_3(TTT)_2F]^{5+}=[C_{98}H_{74}FN_{18}O_4Zn_3]^{5+}$: 356.58; found: 356.68; calcd for $[Zn^{II}_3(TTT)_2]^{6+}=[C_{98}H_{74}N_{18}O_4Zn_3]^{6+}$: 293.99; found: 293.74.

Data for 6: ES-MS: *m/z* calcd for $[Cu^{I}_2Cu^{II}(BBB)(BBT)(BF_4)_2]^{2+}=[C_{76}H_{65}B_2Cu_3F_8N_{13}O_4]^{2+}$: 793.16; found: 793.30; calcd for $[Cu^{I}_2Cu^{II}(BBB)(BBT)(BF_4)]^{3+}=[C_{76}H_{65}BCu_3F_4N_{13}O_4]^{3+}$: 500.62; found: 500.45; calcd for $[Cu^{I}_2Cu^{II}(BBB)(BBT)]^{4+}=[C_{76}H_{65}Cu_3N_{13}O_4]^{+}$: 353.76; found: 353.60; additional peaks: $[Cu^{I}_3(BBB)_2][BF_4]_3$ (**1**); $[Cu^{I}_2Cu^{II}(BBT)_2][BF_4]_4$: calcd for $[Cu^{I}_2Cu^{II}(BBT)_2(BF_4)_2]^{2+}=[C_{80}H_{66}B_2Cu_3F_8N_{14}O_4]^{2+}$: 825.86; found: 825.05; calcd for $[Cu^{I}_2Cu^{II}(BBT)_2(BF_4)]^{3+}=[C_{80}H_{66}BCu_3F_4N_{14}O_4]^{3+}$: 521.64; found: 521.45; calcd for $[Cu^{I}_2Cu^{II}(BBT)_2]^{3+}=[C_{80}H_{66}Cu_3N_{14}O_4]^{3+}$: 369.53; found: 369.43.

Data for 7: ES-MS: *m/z* calcd for $[Cu^{II}_2Cu^{I}(BBB)(TBT)(BF_4)_3]^{2+}=[C_{80}H_{66}B_3Cu_3F_{12}N_{14}O_4]^{2+}$: 869.26; found: 869.20; calcd for $[Cu^{II}_2Cu^{I}(BBB)(TBT)(BF_4)_2F]^{2+}=[C_{80}H_{66}B_2Cu_3F_9N_{14}O_4]^{2+}$: 835.36; found: 835.30; calcd for $[Cu^{II}_2Cu^{I}(BBB)(TBT)(BF_4)_2]^{3+}=[C_{80}H_{66}B_2Cu_3F_8N_{14}O_4]^{3+}$: 550.57; found: 550.60; calcd for $[Cu^{II}_2Cu^{I}(BBB)(TBT)(BF_4)F]^{3+}=[C_{80}H_{66}BCu_3F_5N_{14}O_4]^{3+}$: 527.90; found: 527.90; calcd for $[Cu^{II}_2Cu^{I}(BBB)(TBT)F]^{4+}=[C_{80}H_{66}Cu_3FN_{14}O_4]^{4+}$: 374.17; found: 374.20; calcd for $[Cu^{II}_2Cu^{I}(BBB)(TBT)]^{5+}=[C_{80}H_{66}Cu_3N_{14}O_4]^{5+}$: 295.62; found: 295.67; additional peaks: $[Cu^{I}_3(BBB)_2][BF_4]_3$ (**1**).

Data for 8: ES-MS: no peaks found for the complex $[Cu^{II}_3(BBB)(TTT)][BF_4]_6$ (see text and Supporting Information, Figure S3). $[Cu^{II}_3(TTT)_2][BF_4]_6$: ES-MS: *m/z* calcd for $[Cu^{II}_3(TTT)_2(BF_4)_4]^{2+}=[C_{98}H_{74}B_4Cu_3F_{16}N_{18}O_4]^{2+}$: 1052.80; found: 1052.80; calcd for $[Cu^{II}_3(TTT)_2(BF_4)_3]^{3+}=[C_{98}H_{74}B_3Cu_3F_{12}N_{18}O_4]^{3+}$: 672.93; found: 672.80; calcd for $[Cu^{II}_3(TTT)_2(BF_4)_2]^{4+}=[C_{98}H_{74}B_2Cu_3F_8N_{18}O_4]^{3+}$: 483.00; found: 483.10; calcd for $[Cu^{II}_3(TTT)_2F]^{5+}=[C_{98}H_{74}Cu_3FN_{18}O_4]^{5+}$: 355.48; found: 355.28; calcd for $[Cu^{II}_3(TTT)_2]^{6+}=[C_{98}H_{74}Cu_3N_{18}O_4]^{3+}$: 293.06; found: 293.07.

Data for 9: ES-MS: *m/z* calcd for $[Cu^{II}Cu^{I}Zn^{II}(BBT)(TBT)(BF_4)_3]^{2+}=[C_{84}H_{67}B_3Cu_2F_{12}N_{15}O_4Zn]^{2+}$: 901.71; found: 901.25; calcd for $[Cu^{II}Cu^{I}Zn^{II}(BBT)(TBT)(BF_4)_2]^{3+}=[C_{84}H_{67}B_2Cu_2F_8N_{15}O_4Zn]^{3+}$: 572.21; found: 571.80; calcd for $[Cu^{II}Cu^{I}Zn^{II}(BBT)(TBT)(BF_4)]^{4+}=[C_{84}H_{67}BCu_2F_4N_{15}O_4Zn]^{4+}$: 406.58; found: 406.90; calcd for $[Cu^{II}Cu^{I}Zn^{II}(BBT)(TBT)]^{5+}=[C_{84}H_{67}Cu_2N_{15}O_4Zn]^{5+}$: 308.60; found: 308.45. Additional peaks: $[Cu^{I}_2Zn^{II}(BBT)_2][BF_4]_4$ (**2**); $[Cu^{II}_2Cu^{I}(BBT)_2][BF_4]_5$ (**3**); $[Cu^{I}Zn^{II}_2(TBT)_2][BF_4]_5$ (**4**); 445.1.

Data for 10: ES-MS: *m/z* calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)(BF_4)_4]^{2+}=[C_{89}H_{70}B_4Cu_2F_{16}N_{16}O_4Zn]^{2+}$: 982.19; found: 982.9; calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)(BF_4)_3]^{3+}=[C_{89}H_{70}B_3Cu_2F_{12}N_{16}O_4Zn]^{2+}$: 626.83; found: 626.5; calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)(BF_4)_2F]^{3+}=[C_{89}H_{70}B_2Cu_2F_9N_{16}O_4Zn]^{2+}$: 604.23; found: 604.1; calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)(BF_4)F]^{4+}=[C_{89}H_{70}BCu_2F_5N_{16}O_4Zn]^{2+}$: 431.37; found: 431.3; calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)F_2]^{4+}=[C_{89}H_{70}Cu_2F_2N_{16}O_4Zn]^{2+}$: 414.52; found: 414.1; calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)F]^{5+}=[C_{89}H_{70}Cu_2FN_{16}O_4Zn]^{2+}$: 327.81; found: 327.6; calcd for $[Cu^{II}_2Zn^{II}(BBT)(TTT)]^{6+}=[C_{89}H_{70}Cu_2N_{16}O_4Zn]^{6+}$: 270.01; found: 269.9; additional peaks: $[Zn^{II}_3(TTT)_2][BF_4]_6$ (**5**); $[Cu^{II}(BBT)][BF_4]_2$: calcd for $[Cu^{II}(BBT)(BF_4)]^{+}=[C_{40}H_{33}BCuF_4N_7O_2]^{+}$: 793.20; found: 793.2; calcd for $[Cu^{II}(BBT)]^{2+}=[C_{40}H_{33}CuN_7O_2]^{2+}$: 353.64; found: 353.45.

Data for 11 : ES-MS: no peaks found for the complex $[Cu^{II}Zn^{II}_2(TBT)(TTT)][BF_4]_6$. $[Zn^{II}_3(TTT)_2][BF_4]_6$ (**6**); $[Zn^{II}(TBT)][BF_4]_2$: calcd for $[Zn^{II}(TBT)]^{2+}=[C_{44}H_{34}BF_4N_8O_2Zn]^{+}$: 857.21; found: 857.2; calcd for $[Zn^{II}(TBT)]^{2+}=[C_{44}H_{34}ZnN_8O_2]^{2+}$: 385.10; found: 385.2.

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