Supramolecular Chemistry

Dynamic Helicates Self-Assembly from Homo- and Heterotopic Dynamic Covalent Ligand Strands

Antonio Santoro,[a, b] Jan Holub,[a, c] Marta A. Fik-Jaskółka,[a, d, e] Ghislaine Vantomme,[a, f] and Jean-Marie Lehn*[a]

Abstract: The understanding and the application of reversible covalent reactions and coordination chemistry together with the proper design of the molecular frameworks, allow to achieve not only well-defined output architectures but also different grades of complex behavior. In this work, the dynamic nature of the helical systems offers an additional level of complexity by combining self-sorting on two levels: 1) the build-up of the ligand strand constituents from their components through dynamic covalent chemistry; 2) the assembly of the helicates from the ligands and the metal cations through dynamic metallo-supramolecular chemistry. The information encoded in the ligands constituent molecule was read differently (and accurately at the same time) by metal cations that varied in the coordination algorithms. It enabled the selective formation of a specific type of helicates from a wide library of helicates formed by the possible combination of subcomponents. Ligands containing dynamic tridentate and/or bidentate binding motifs in the same strand were studied to explore the helicates self-assembly with appropriate metal cations.

Introduction

The aesthetic features of helical geometry fascinated humans from time immemorial becoming one of the central motifs of human art and architecture. However, its utility is wide beyond the aesthetics, nature made it in the shape of helical doubly wrapped DNA molecule arguably the most important and famous structure among the molecules of life on the planet earth.[1]

Helical motive has also intrigued attention of the modern chemists, who have designed countless molecules specifically to combine its chemical and spatial features in practical „artificial“ chemical systems. Indeed, chemistry offers opportunities to explore approaches that are different from those present in the molecules of living organisms or so called *abiotic* helical molecular entities. Whereas the assembly of biological supramolecular structures makes mainly use of organic non-covalent interactions (hydrogen donor-acceptor interactions, Van der Waals forces), metal ion binding provides a variety of coordination geometries which offer a rich set of connection patterns. A very broad range of binding strengths and formation kinetics can be explored depending on the nature of the metal cation and the ligand binding sites. Moreover, different metal cations offer the possibility to alter the electronic and binding properties through the external physical stimuli such as light or electricity.[2,3]

Variation of ligand structure and metal cation has already provided plethora of highly complex metallo-supramolecular architectures.[2,3] The importance of these entities is related more generally to the development and understanding of self-organization processes in supramolecular chemistry, through the design of programmed metallo-supramolecular architectures. The term "programmed" is here meant for multicomponent self-assembling processes involving the reading of molecular information in organic ligands and its processing through interactional algorithms defined by the cation coordinational

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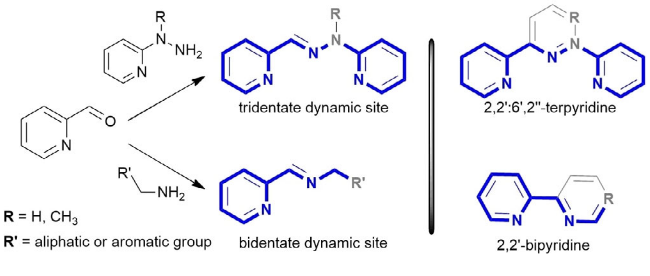
preferences/patterns.[2,4] The output of the full programming process is then manifested by the assembly of a particular structure.

Since the initial generation of a trinuclear double helicate from a strand of three 2,2′-bipyridine (**B**) subunits and Cu^I cations,[6] numerous imaginative studies have been conducted widely extending the field, inter alia to multiple linear helicates[5] as well as circular helicates[7] and many other structural types (including catenates, knots, etc.[3e–g, 11]). Strands based on terpyridine (**T**) groups and mixed **B**, **T** strands were implemented as well as extensions to other types of bidentate and tridentate sites.[5,8]

The complexity of various types of helicates can be simply sorted out by the individual structural features.[2,5] Ligands containing only one type of coordination subunit may be referred to as homotopic and heterotopic if they present different motifs. The resulting helicates are termed homostranded when containing identical ligand strands, and heterostranded when they incorporate different ligands. They may also be doubly hetero-structural if they contain at the same time different coordination subunits and different strands,[8,9] thus providing the intriguing complexity for different information encoding in molecules.[9]

The active development of the field of dynamic covalent chemistry (DCC)[10] also penetrated the area of coordination chemistry leading to three types of implementations in ligand design: 1) ligands containing multiple coordination subunits connected by reversible covalent connections;[12] 2) dynamic coordination subunits formed by reversibly linked mono- or bidentate binding groups;[13] 3) a combination of 1) and 2) resulting in multiple dynamic ligands. Typical examples of case 2) are bidentate NN and tridentate NNN units based on the formation of a dynamic covalent link by condensation of a respective amine (imine link) or hydrazine (hydrazone link) with pyridine-2 carboxaldehyde (Scheme 1).

The presence of the reversible covalent bond in the coordination subunit of the ligand offers the possibility to drive the assembly of both ligands and the metallo-supramolecular architecture by the coordination process itself. There are at present only few examples reported of assemblies of dynamic multitopic (>2 subunits) ligands which are at the same time also heterotopic, that is, contain different coordination subunits.[14]



Scheme 1. Generation of dynamic bidentate **B** and tridentate **T** metal cation coordination subunits (dynamic analogues of bipy **B** and terpy **T**) by reversible condensation of an aldehyde with an amine or a hydrazine derivate, respectively.

The work described here concerns especially architectures combining the three general features presented above: 1) being metallo-supramolecular, thus metallo-dynamic; 2) presenting helical structures; 3) involving dynamic covalent ligand strands. It introduces the features of DCC into covalently static heterotopic ligands and helicates.[8] The aim here was to design dynamic heterotopic ligand strands displaying bidentate NN and/or tridentate NNN binding sub-units and incorporating reversible covalent C=N bonds and explore their double helical self-assembly into different metallo-supramolecular entities through the appropriate ligand–metal interactions. The ligand strands will be designated by the sequence of their **B** and **T** motifs or of their dynamic counterparts **B** and **T** presenting, respectively a reversible imine and hydrazone connection (Scheme 1).

Results and Discussion

Dinuclear Semi-dynamic and Dynamic Ligands and their Helicates

At first, the binding properties of dynamic heterotopic ligands presenting two binding pockets were studied. The semi-dynamic ditopic ligand **BT-1** constituted from a non-dynamic bypiridine moiety (**B**) linked to a dynamic tridentate (**T**) hydrazone subunit of Paphy-type (pyridine-2-aldehyde 2′-pyridylhydrazone) (Figure 1)[5a, 14a, 15] was synthesized and its helical assembly studied in presence of various metallic cations. The multiple binding sites offer opportunities to read the coordinational code of **B** and **T** depending on the metallic cations used. As the metal cation properties differ so does the output, in our case from the single to double stranded helices.

The treatment of a suspension of herein depicted **BT-1** ligand in acetonitrile (ACN) with a 1:1 solution of Zn^{II} and Cu^I (both as triflate salts ($[OTf]^-$), in acetonitrile, 0.5 equivalents of each in regard to the ligand) led to formation of the heterotopic helicate with head to head orientation. The ^1H NMR spectrum showed the expected splitting of the signal of the four

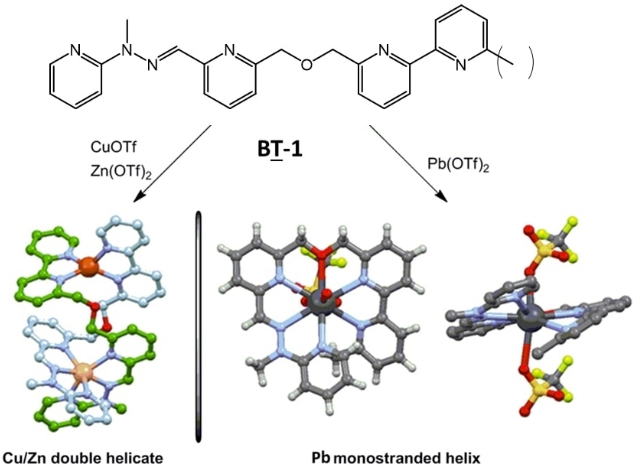
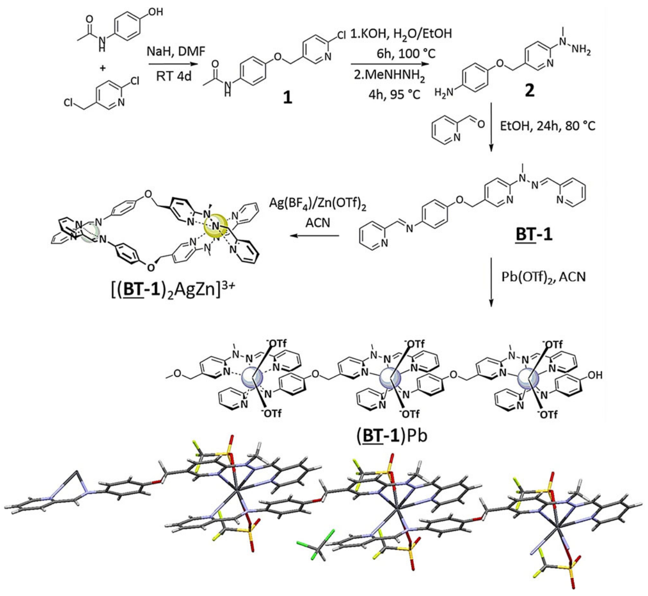


Figure 1. Ditopic semi-dynamic ligand **BT-1** and its helicates: heteronuclear double helicate (left) and single helicate (right).

diastereotopic protons belonging to the connector of the two binding units. This splitting comes from the chiral nature of the asymmetric spatial environment around double helical assembly (see Supporting Information). The head to head arrangement was subsequently confirmed with single-crystal X-ray crystallography.[24] The two ligands are wrapped around the two metal ions, with the Zn^{II} ion in octahedral coordination with the two tridentate sites **T** and the Cu^{I} ion in tetrahedral coordination with the two bidentate **B** moieties (Figure 1). In contrast, the self-assembly of **BT-1** in presence of a coordinatingly less stringent cation such as Pb^{II} results in the formation of a single stranded complex with a single-ligand strand helically wrapped around metal (Figure 1).

The subsequent step concerned the study of a fully dynamic ditopic ligand containing a **B** and a **T** coordination site (**BT**). The synthetic pathway involved a Williamson reaction to generate an ether bridge, heating with methyl hydrazine to obtain the hydrazino derivative and condensation with 2-pyridine aldehyde to afford final **BT-1**. Treatment of this ligand with Zn^{II} and Ag^{I} triflate salts (each 0.5 equiv. in regard to ligand) in acetonitrile gave a sharp and well resolved ^1H NMR spectrum which indicated the presence of well-defined complex in the solution. Despite the lack of crystallographic evidence, based on NMR and HRMS the complex was determined to be doubly helical $[(\mathbf{BT\text{-}1})_2AgZn]^{3+}$ species (Scheme 2, Supporting Information). Further, the DOSY obtained volume of 2873 $Å^3$ for $((\mathbf{BT\text{-}1})_2AgZn)^{3+}$ well matches the calculated value of 2700 $Å^3$ (see Supporting Information). The 2D NMR analysis data confirmed that the paphy **T** unit and imine **B** unit are selective towards each metal ion according to their coordination properties (See Supporting Information). Again, applying a metal cation with different spatial preferences led to the alternation of the reading process and consequently alternation in the output. This time the addition of Pb^{II} led to the formation of 2D coordination polymer instead of a defined molecular complex as in the case of **BT-1**. This example illustrates the intricacies of the coding/reading process as any slight change in the spatial arrangement of the binding units can in some cases indirectly alter the output as well.



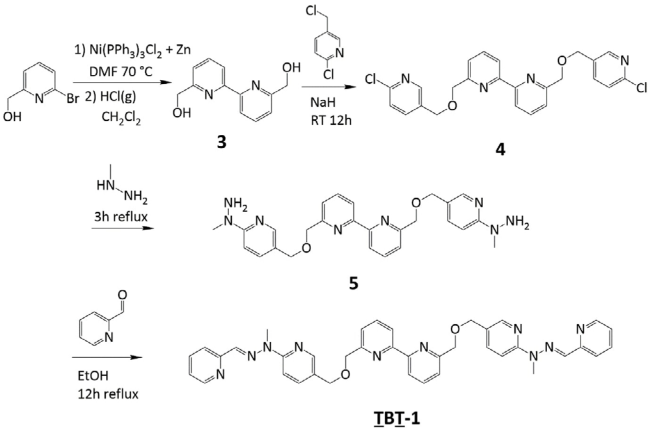
Scheme 2. (Top) Synthesis of ligand **BT-1**. (Middle left) representation of the complex $[(\mathbf{BT\text{-}1})_2AgZn]^{3+}$. (Bottom) Representation and X-ray structure of the coordination polymer formed in the presence of $Pb^{II}(OTf)_2$.

Tritopic Semi-dynamic Ligands with Terminal Hydrazine Core and their Trinuclear Octahedral Helicates

As it was mentioned in the introduction, there are only a few examples of dynamic multinuclear helicates. Heterotopic dynamic ligands with >2 coordination pockets are even more scarce.[11e,14c–d] We decided to synthesize a small set of semi-dynamic ligands, that is, ligands containing a non-dynamic central unit of **T** or **B** type bearing branches with imine **B** or hydrazone **T** based dynamic coordination subunits.

As a first example, the heterotopic ligand **TBT-1** with a central **B** core and terminal hydrazine groups was synthesized as shown in Scheme 3. The synthetic path consisted in the formation of the derivative **3** by nickel catalysed cross coupling reaction with the product precipitating as hydrochloride salt. The next step involved a Williamson reaction of the bis-alkoxide of **3** to obtain compound **4**. Treating **4** with methylhydrazine then gave **5** in high yield (95 %). Finally, the condensation of **5** with a pyridine 2-carboxaldehyde yielded **TBT**-1 (See Supporting Information).

We tested the reaction of this ligand with different sets of metal ions. The best assembly was achieved treating 1 equivalent of the ligand with 1 equivalent of $Zn(OTf)_2$ or $Fe(OTf)_2$ and 0.5 equivalents of CuOTf. In both cases, the formation of a colored limpid solution was observed after the addition of the metal ion solutions into a suspension of the ligand in acetonitrile. Heating the solution at 60 °C for a week gave no significant spectral changes, which suggests that the complex formed in solution was already the thermodynamically most stable product, under the conditions used. The mass spectroscopy strongly suggested the presence of the $(\mathbf{TBT\text{-}1})_2M_2Cu$ (M = Zn or Fe) complex in the solution. In addition, the splitting of the diasterotopic oxypropylene protons (-CH_2-*O*-CH_2-) signals observed in ^1H NMR spectra was indicative of the asym-



Scheme 3. Pathway followed for the synthesis of the ligand **TBT-1**.

metric spatial environment typical for a helical structure.[6] Final confirmation came from the single-crystal X-Ray analysis.[24] Interestingly, two different sets of crystals were obtained from the same crystallization setup. Liquid diffusion of diisopropyl ether into an acetonitrile solution of **TBT-1**, Cu^I and Zn^{II} provided orange crystals as well as colorless needles. The orange crystals showed to be the heterotopic trinuclear Zn^{II}/Cu^I double helicate (**TBT-1**)$_2$Zn$_2$Cu ($R1 = 9.85\,\%$) with one tetrahedral Cu^I in the middle and two octahedral Zn^{II} on the sides (Figure 2, bottom). The colorless needles were identified as the helicate (**TBT-1**)$_4$Zn$_6$ ($R1 = 7.65\,\%$) of circular type shown in Figure 2, left. This structure consists of four ligands wrapped around six Zn^{II} cations. The coordination motif of the Zn^{II} cations in the central **B** unit is quite interesting. The proximity of the -CH_2OCH_2- linker to the **B** unit allows for the oxygen to bind to the central Zn^{II} metal ion in the structure of (**TBT-1**)$_4$Zn$_6$. Therefore, the binding motif around Zn^{II} consists of five nitrogen sites (from the **B** and MePaphy units) and one ether oxygen (from the linker). Subsequently, the two described species (**TBT-1**)$_2$Zn$_2$Cu and (**TBT-1**)$_4$Zn$_6$ could be prepared and crystalized separately using precise amounts of appropriate cation(s). Unfortunately, the full bottom-up dynamic assembly of the double helicate from the ligand components (the central unit **5**, 2-pyridinecarboxaldehyde and the metal cations) failed as an initially formed red-orange **(5)$_2$Cu**$^+$ complex underwent rapid oxidation into a green Cu^{II} complex in the presence of the hydrazine. Because of the possible penta-coordinating site in the circular helicate, it appeared of interest to insert Cu^{II} cations which display preference for this coordination number.[16] In fact, by using a 2:2:1 Ligand:Cu^{II}:Zn^{II} mixture, a complex with the same ratio of metal cations was obtained. This is a rare example of a hexanuclear heterometallic (Cu^{2+} and Zn^{2+}) circular helicate, obtained by a self-assembly approach (for hetero-self-assembling systems see also references[8] and[17]). The structure of this species was confirmed by X-ray crystallography and is shown in Figure 2.[24]

The very appealing feature of these semi-dynamic ligands is their tunability: the simple variation of the capping unit makes it possible to generate ligands with either **B** or **T** units in the terminal coordination pockets.

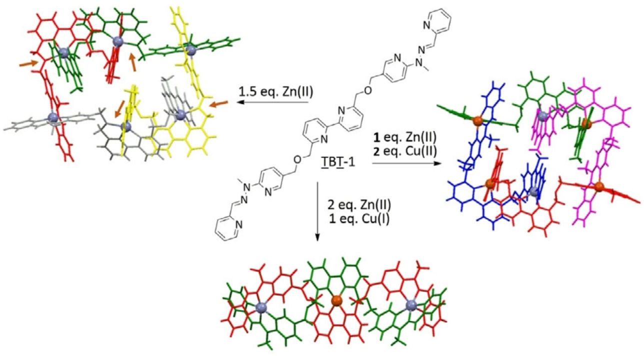


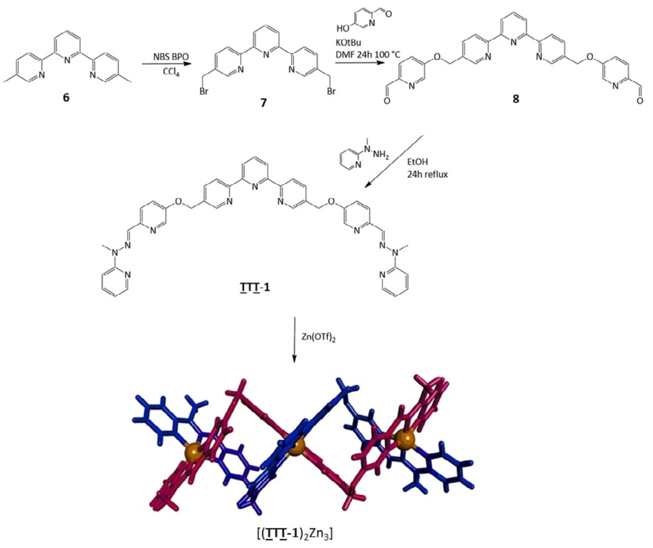
Figure 2. Generation of three different helicates from ligand **TBT-1** and different sets of metal cations. (Left) Representation of the circular helicates formed by **TBT-1** with Zn^{II} alone; the interaction of one oxygen from the linker with the Zn^{II} in the central **B** unit is indicated by an arrow. (Right) Circular helicate formed by using a mixture of Zn^{II} and Cu^{II}. (Bottom) Structure of the trinuclear double helicate (**TBT-1**)$_2$Zn$_2$Cu.

Tritopic Dynamic Ligands with Terminal Aldehyde core and their Trinuclear Octahedral Helicates

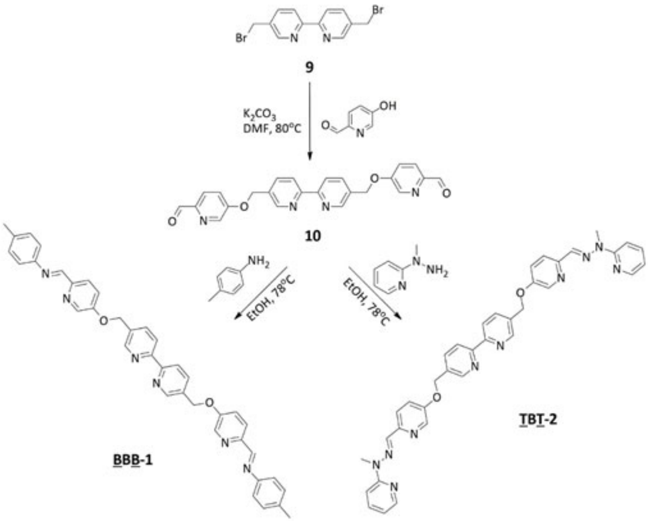
To increase the versality and tunability of our ligands, the next generation was designed with core moiety decorated with terminal aldehyde groups instead of hydrazine ones. This change allows to use both amines as well as hydrazines thus enables better on-demand customization of the ligand. A series of different heterotopic (**TBT**) and homotopic (**BBB** and **TTT**) ligands were prepared as the aldehyde functional groups in the central subunit allows the use of different capping units. Herein, we used 2-(1-methylhydrazino) pyridine, benzhydrazide and *p*-toluidine. To complement these ligands with a central **B** unit, a similar series of ligands was synthesized from the strand **8** containing a central **T** unit and terminal 2-pyridinecarboxaldehyde moieties. Condensation of **8** with 2-(1-methylhydrazino) pyridine then provided final ligand **TTT-1** (Scheme 4).

Treatment of this ligand strand with 1.5 equivalents of Zn^{II} and Cd^{II} afforded complexes which all gave clear, well-resolved ^{1}H NMR spectra and ESI-MS confirmed their identity as trinuclear double helicates. This architecture was corroborated by a single-crystal X-ray structure determination of **(TTT-1)$_2$Zn$_3$** ($R1 = 9.5\,\%$, Scheme 4).[24] It showed the expected double helical structure where the ligands fold around three Zn^{II} cations in octahedral coordination. Next, we explored the formation of trinuclear helicates from the tritopic dynamic ligand **BBB-1** which was obtained following the synthetic protocol shown in Scheme 5.

The obtained ligand **BBB-1** shows two bidentate „bipy-like“ dynamic units connected to the central moiety. When mixed with Zn^{II} solution, the expected (**BBB-1**)$_3$Zn$_3$ triple-helicate was obtained. However, treating the same ligand with Cu^I did not afford any defined species, according to ^{1}H NMR of the mixture



Scheme 4. Synthetic protocol towards the ligand **TTT-1** and representation of the **(TTT-1)$_2$Zn$_3$** solid state structure.



Scheme 5. Pathway for the synthesis of **BBB-1** and **TBT-2** ligands.

(Figure 3). This result is in agreement with the former studies using covalent ligands and supports the hypothesis that connection of the bridge in the position 5 of the central **B** unit is too rigid to allow wrapping around the tetra-coordinating metals into a double helicate.[5a,18]

Differently to **BBB-1**, the ligand **TBT-2** was obtained by the reaction of the di-aldehyde (**10**) core with 2-(1-methylhydrazinyl)pyridine, using the same reaction conditions as mentioned above for **TTT-1** (Scheme 5). The ligand **TBT-2** shows the same central bidentate core and bridges of **BBB-1**, but this time with two tridentate hydrazone pockets on the sides. Figure 4 shows **(TBT-2)$_2$Zn$_2$** complex, obtained by mixing component **10** with Zn^{II} and 2-(1-methylhydrazino)-pyridine as capping unit. ^{1}H NMR and MS (851.1504 for ([[**TBT-2**]$_2$**Zn$_2$(OTf)$_3$**]$^{2+}$) data obtained suggest the presence of a species with two Zn^{II} ions linked to the **T** „peripheral" subunits and without any metals coordinated to the central **B** subunit. It is worth mentioning that the absence of a split signals of oxypropylene protons in ^{1}H NMR clearly indicate the absence of a helical complex in solution.

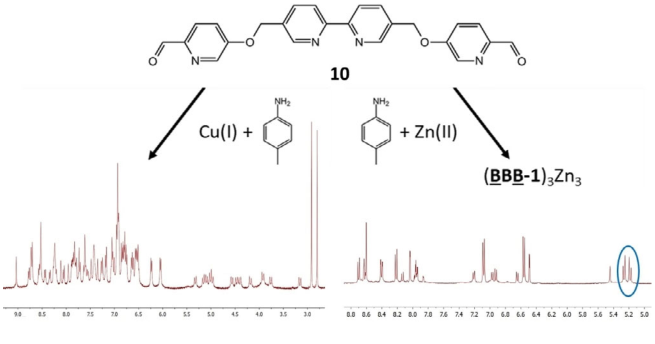


Figure 3. ^{1}H NMR spectra of the solutions obtained by treating **10** with *p*-toluidine (2 equiv.) and either 1.5 equiv. of Cu^I or 1 equiv. of Zn^{II} triflate in ACN-d$_3$. The splitting signals of the oxypropylene protons due to the helix formation was evidenced with a blue circle.

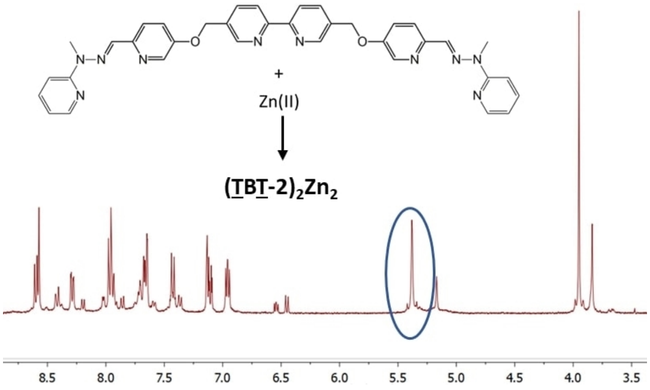


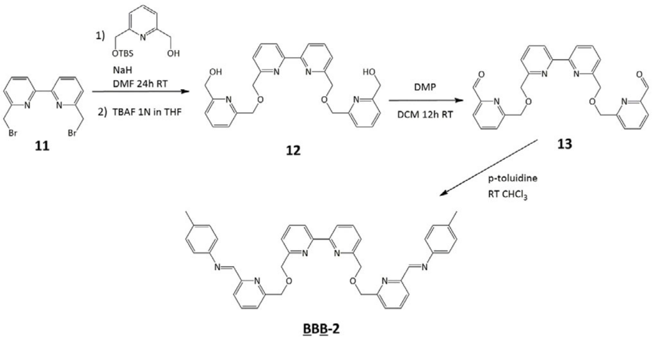
Figure 4. ^{1}H NMR spectra of the double helicate (**TBT-2**)$_2$Zn$_2$ formed in a mixture of 2 equiv. of **10**, 3 equiv. of Zn^{II} triflate salt and 4 equiv. of 2-(1-methylhydrazino)-pyridine as capping unit in ACN-d$_3$. The signal of the protons -CH$_2$-*O*- was evidenced with a blue circle. The peak at around 4 ppm is due to the methyl of the hydrazone.

Tritopic Dynamic Ligand with a Terminal Aldehyde Core and its Tetrahedral Trinuclear Helicates

The analogous ligand **BBB-2** was prepared in a similar way to **TBT-1**, only with a non-dynamic **B** unit in the center and two terminal dynamic **B** coordination pockets (see Scheme 6).

The synthetic pathway starts with the formation of 6,6'-dimethyl **B** derivative through cross-coupling reaction[19] and subsequent bromination with NBS. The brominated product was then reacted with a mono-silyl protected pyridine diol. The fluoride catalysed deprotection followed with Dess–Martin oxidation afforded the symmetrical bis-aldehyde core **13** (Scheme 6). The ligand **BBB-2** was finally obtained via condensation of **13** with *p*-toluidine. The synthetic procedure is reported in the Supporting Information (page 25).

Treatment of **BBB-2** with Cu^I triflate, in 2:3 ratio, afforded a trinuclear double helicate displaying the expected splitting signals of bridging -CH$_2$-*O*- between 3.70 to 4.03 ppm in NMR and the mass-to-charge ratio of 802.15 ([(**BBB-2**)$_2$**Cu$_3$(OTf)**]$^{2+}$) in mass spectroscopy. When **BBB-2** is mixed with a solution of Zn^{II} triflate (in 1:1 ratio), the ^{1}H NMR spectrum also shows the characteristic signals for the helical species (splitting of the signals of oxypropylene protons). However, the MS data suggests the complex consists of only one ligand wrapped around a Zn^{II} ion (([(**BBB-2)Zn(OTf)**]$^+$ with a mass-to-charge ratio of 845.17).



Scheme 6. Pathway for the synthesis of **BBB-2**.

This suggests that the connection to the central **B** unit at 6,6′ positions fails to give a triple-stranded helicate, probably as a result of steric crowding around the metal ions.[5a,18] Unfortunately, so far it was not possible to obtain a single crystal to confirm the actual constitution with X-ray diffraction.[24] The behavior of these two complexes is represented in Figure 5.

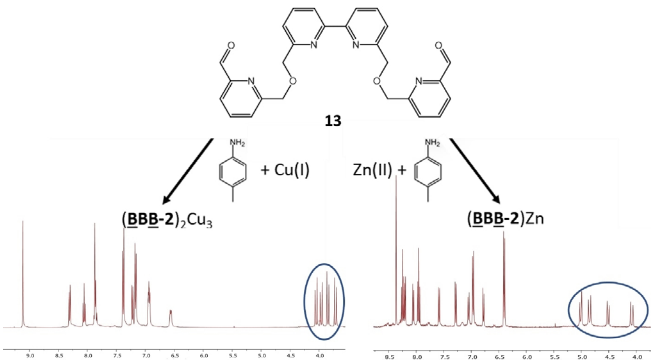
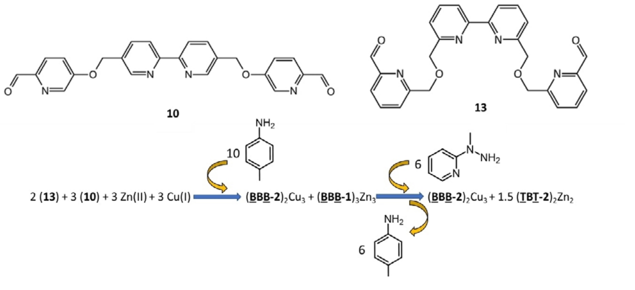


Figure 5. ^{1}H NMR features of the solutions obtained by treating **13** with *p*-toluidine (2 equiv.) and either 1.5 equiv. of Cu^I or 1 equiv. of Zn^{II} triflate in ACN-d_3. The splitting signals of the oxypropylene protons due to the helix formation was evidenced with a blue circle.

Self-recognition/ Homo-self-sorting in Libraries of Dynamic Helicates

In recent years, self-sorting processes have gained the spotlight as a means of effective molecular construction and smart chemical system operation, in particular in (metallo-)supramolecular chemistry[20] and/or in DCC.[21] The simplest example of a self-sorting process involved double selection of both ligand strands and metal ion in the self-assembly of helicates. It was driven by self-recognition and may be considered as a homo-self-sorting process.[20a] It involved the dynamic generation of the „correct“ double and triple helicates from a mixture of covalent polypyridine ligands driven by the coordination properties of metal cations (Ni^{II} vs. Cu^I) and by the structure of the ligand back bone. The dynamic ligands described here offer an additional level of complexity by combining self-sorting on two dynamic levels: 1) the build-up of the ligand strand constituents from their components through dynamic covalent chemistry; 2) the assembly of the helicates from the ligands and the metal cations through dynamic metallo-supramolecular chemistry.

The two components **10** and **13** represented in Scheme 7 were chosen to produce semi-dynamic ligand strands and explore their features in the assembly of dynamic helicates. These strands (**10** and **13**, respectively) differ in the connection between the core and the branches from position 5,5′ to 6,6′ and in the rigidity of the bridging connections. Both ligands combined with *p*-toluidine as capping unit provide a semi-dynamic ligand of **BBB** design.



Scheme 7. Overview of the double self-sorting process on the dynamic covalent and metallo-supramolecular formation of dynamic helicates.

When both **10** and **13** were mixed together and treated with 2 equivalents of *p*-toluidine and the appropriate amount of Cu^I and Zn^{II} triflates (the exact ratio is shown in the Figure 6), only two species were observed in solution (Scheme 7). The ^{1}H NMR of the mixture of components clearly displayed the combination of the correctly homo-self-sorted (**BBB-2**)$_2$Cu$_3$ and (**BBB-1**)$_3$Zn$_3$ helicates. No other possible species, such as heterometallic or heterostranded helicates, were detected. (Figure 6).

The subsequent addition of 2 equivalents of 2-(1-methylhydrazino)-pyridine in this self-sorted system led to a new thermodynamic equilibrium manifested by the redistribution of the components. The hydrazine unit is able to exchange the amine forming stronger hydrazone bond compared to the

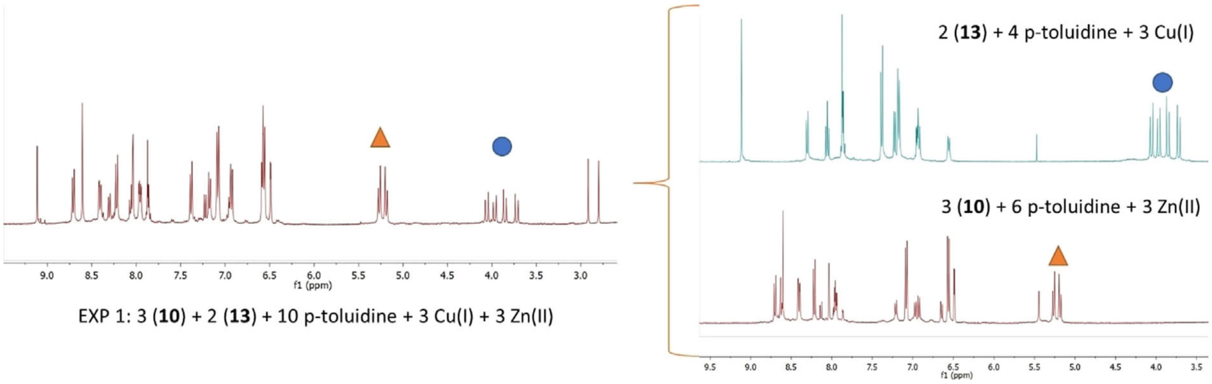


Figure 6. (left) ^{1}H NMR spectrum obtained by mixing 3 (**10**) + 2 (**13**) + 10 *p*-toluidine + 3 Cu^I + 3 Zn^{II}. It is the combination of the ^{1}H NMR spectra registered from the double (**BBB-2**)$_2$Cu$_3$ and triple (**BBB-1**)$_3$Zn$_3$ helicates (shown on right side).

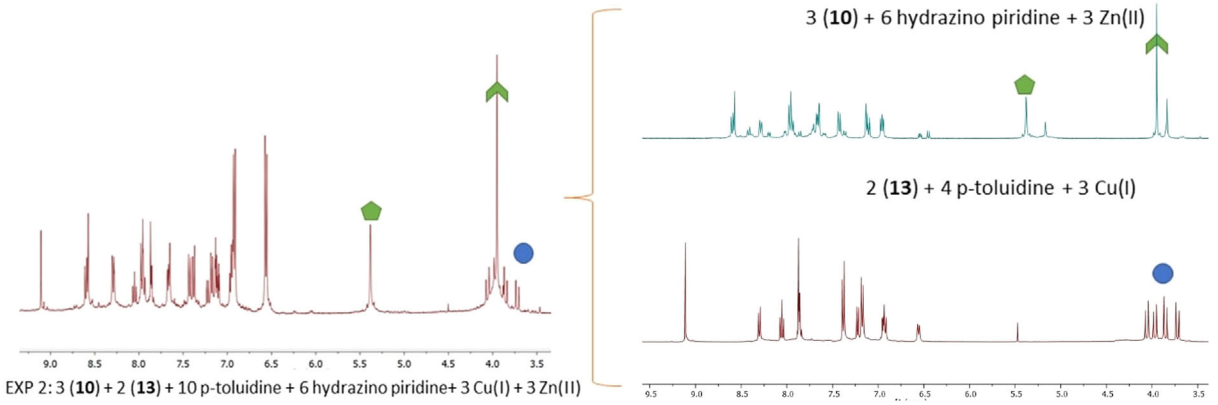


Figure 7. (left) ^{1}H NMR spectrum obtained by mixing 3 (**10**) + 2 (**13**) + 10 *p*-toluidine + 6 hydrazino pyridine + 3 Cu^I + 3 Zn^{II}. It is the combination of the spectra registered from the (**BBB-2**)$_2$Cu$_3$ and (**TBT-2**)$_2$Zn$_2$ species (shown on right side).

former imine. Due to the different steric requirements of the different assemblies described above, the 2-(1-methylhydrazino)-pyridine replaced only the *p*-toluidine unit involved in the formation of the triple helix (**BBB-1**)$_3$Zn$_3$ thus favoring the bridging connections at the position 5,5′ of the core unit. The result is a formation of a new (**TBT-2**)$_2$Zn$_2$ species with a hexacoordinated double NNN tridentate pocket at each side whereas the other double helicate (**BBB-2**)$_2$Cu$_3$ was left unchanged. (Figure 7). These results thus represent the double homo-self-sorting process, or double self-recognition[19] process, involving two dynamic levels: 1) dynamic covalent exchange in the build-up of the ligand constituents from their components; 2) dynamic coordinative in the assembly of the helicates from the ligands and the metal cations.

Conclusions

Information stored in molecular systems plays a key role in the self-organization of supramolecular and dynamic covalent functional architectures. The information encoded in a dynamic ligand constituent molecule is read differently (and accurately at the same time) by metal cations that vary in the coordination algorithms, so as to lead to the formation of the correct ligand under the driving force of the coordination features of the given metal-ligand combination. The cation coordination algorithms read the molecular structural information (codons) of the dynamic organic ligands forming the „virtual“ dynamic library[10a] of the constituents that are accessible to form in situ from the available components. When supplemented with new components presenting different structural features, the system rearranges (corrects) itself (triple vs. double helicate) thus undergoing adaptation.[22] The process results in the generation of various outputs that may differ significantly (helicate vs. pincer-type complex[9] and double helicate vs. circular helicate[9]). Combining it with the ability of reading new information (an input component) and self-correction of the system (yielding another output) makes it a powerful tool towards the design of complex chemical systems.[23]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: double-helical structures · dynamic covalent chemistry · metallo-supramolecular structures · programmed self-assembly

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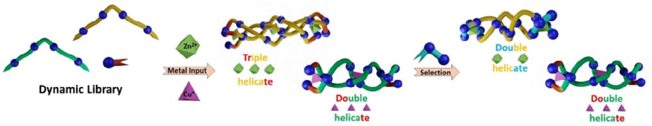
FULL PAPER



Keep it dynamic: The dynamic nature of the helical systems offers an additional level of complexity by combining self-sorting on two levels: 1) the build-up of the ligand strand constituents from their components through dynamic covalent chemistry; 2) the assembly of the helicates from the ligands and the metal cations through dynamic metallo-supramolecular chemistry.

Supramolecular Chemistry

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Dynamic Helicates Self-Assembly from Homo- and Heterotopic Dynamic Covalent Ligand Strands