Self-Sorting of Two Imine-Based Metal Complexes: Balancing Kinetics and Thermodynamics in Constitutional Dynamic Networks

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A major hurdle in the development of complex constitutional dynamic networks (CDNs) is the lack of strategies to simultaneously control the output of two (or more) interconnected dynamic processes over several species, namely reversible covalent imine bonds formation and dynamic metal-ligand coordination. We have studied in detail the factors influencing the fidelity of the self-sorting process (concentration, electronic and steric parameters of the organic components, nature of the metal cations) of 11 constitutional dynamic libraries containing two different amines, aldehydes and metals salts into two imine-based metal complexes, having no overlap in term of their compositions. In all the cases, the outcome of the process was primarily determined by the ability of the octahedral metal ions to select its pair of components from the initial pool of components, the composition of the weaker tetrahedral complex being imposed by the components rejected by the octahedral metal ions. Different octahedral metal ions required different level of precision in the “assembling instructions” provided by the organic components of the CDN to guide it towards a sorted output. The concentration of the reaction mixture, the electronic and steric properties of the initial components of the library were all found to influence the lifetime of unwanted metastable intermediates formed during the assembling of the two complexes.

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Self-sorting of two imine-based metal complexes: balancing kinetics and thermodynamics in constitutional dynamic networks

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Abstract

A major hurdle in the development of complex constitutional dynamic networks (CDNs) is the lack of strategies to simultaneously control the output of two (or more) interconnected dynamic processes over several species, namely reversible covalent imine bonds formation and dynamic metal-ligand coordination. We have studied in detail the factors influencing the fidelity of the self-sorting process (concentration, electronic and steric parameters of the organic components, nature of the metal cations) of 11 constitutional dynamic libraries containing two different amines, aldehydes and metals salts into two imine-based metal complexes, having no overlap in term of their compositions. In all the cases, the outcome of the process was primarily determined by the ability of the octahedral metal ions to select its pair of components from the initial pool of components, the composition of the weaker tetrahedral complex being imposed by the components rejected by the octahedral metal ions. Different octahedral metal ions required different level of precision in the “assembling instructions” provided by the organic components of the CDN to guide it towards a sorted output. The concentration of the reaction mixture, the electronic and steric properties of the initial components of the library were all found to influence the lifetime of unwanted metastable intermediates formed during the assembling of the two complexes.
Introduction

Rivalling with the intricacy of biological processes in the construction and the exploitation of complex networks of molecules requires the development of new synthetic strategies to control the organization of large sets of molecules having a wide compositional and interactional diversity.\cite{1} To this end, the notions of orthogonal self-assembly\cite{2} and self-sorting\cite{3-7} are cornerstones of these strategies, especially when applied within the context of constitutional dynamic chemistry (CDC), based on molecules capable of adapting their constitution by exchange of their reversibly linked components.\cite{1-8,8,9}

By addressing chemical systems at both molecular and supramolecular levels, CDC provides a convenient way to organize complex dynamic systems and consequently to control their properties. Constitutional dynamic libraries (CDLs) operating via the reversible condensation of amine- and 2-formylpyridine-containing components into dynamic imine-based constituents acting as ligands for transition metal cations have unlocked the path toward architectures that would otherwise be inaccessible by traditional synthetic means and capable of displaying complex properties (e.g. feedback loops, adaptation, etc.).\cite{7e-i,9b-e,10,11} It was shown that the simultaneous assembly of several type of such constitutional dynamic architectures within the same reaction mixture allowed for the emergence of new properties going beyond those of each individual architecture,\cite{11n,6d,9d,e,11a-d,q} highlighting a link between increased compositional diversity and diversification of the displayed properties. However, to date, the compositional diversities of “poly-architecture” constitutional dynamic systems are limited. The systems reported in the literature involve architectures which always have at least one or two reagents in common (i.e. organic components and/or type of metal cations), thus limiting their potential in terms of compositional diversification and properties. One major hurdle in the development of more diverse systems is the lack of strategies to simultaneously control the outcome of two (or more) interconnected dynamic processes over several architectures, namely reversible covalent imine bonds formation and dynamic metal-ligand coordination.

Here we investigate the simultaneous generation of 11 different pairs of fully non-identical imine-based metal complexes via the self-sorting of their six initial building blocks. The study provides insights into the factors influencing the fidelity and the rate of such self-sorting processes and points at the interplay between thermodynamic driving forces and kinetic traps in the self-assembly of constitutional dynamic systems.

Results and Discussion

a. Rationale and initial design

Factors such as the denticity, the steric bulk and the electronic properties of a ligand can be exploited to tune its binding strength with a given type of transition metal, as each transition metal has well-defined coordination preferences due to its unique electronic makeup.\cite{12} The formation of a given imine-containing ligand constituent from a library of amine and aldehyde components can be selectively promoted via its preferential binding to one type of transition metal, if this constituent offers the best coordination environment for this metal cation out of all the possible combinations of the initial components.\cite{11-n,8,9} The same principle can be extended to the simultaneous but selective generation of two (or more) imine-containing ligand constituents if two (or more) types of transition metals having different coordination preferences are used.\cite{9e,f}
A difference between metals of tetrahedral and octahedral coordination geometries exploitable by appropriate ligand design is that the former can be considered to involve two orthogonal planes containing two donor atoms whereas the latter involves two orthogonal planes with three donor atoms. Thus, by choosing amine and aldehyde reactants giving either a planar bidentate or a planar tridentate chelate by imine condensation, selectivity results in that full coordination of the former forms a tetrahedral species while that of the latter yields an octahedral one. Where the donor atoms of both ligands are similar (or identical) and the concentrations of both are the same, the higher denticity of the tridentate ligand should lead to a chelate-type binding strongly favouring its binding to a metal ion of octahedral coordination geometry. For such reasons, the condensation of aniline derivative 1 (Figure 1) with a 2-formylpyridine was expected to give a ligand suited to coordination of tetrahedral Cu(I) center, while condensation of the aminoquinoline derivative 2 was expected to give a ligand suited to coordination of octahedral Fe(II) center.

The pairing of Fe(II) with one of the two derivatives of 2-formylpyridine can be inhibited by manipulating the steric hindrance around the coordination site of its pyridine. The coordination of the three nitrogen nuclei of 2,2':6',2''-terpyridine-like ligands—such as the ligands obtained by the condensation of the aminoquinoline 2 with derivatives of 2-formylpyridine—to an octahedral metal ion is known to induce a “pinching” of these ligands resulting in a contraction of the distance between their positions 6 and 6". Any congestion in these positions will destabilize the resulting complex. Consequently, Fe(II) should favor the inclusion of 2-formylpyridine 3 (Figure 1) in its coordination sphere as it bears less steric hindrance than its peer 4.

This rationale was tested by mixing components 1, 2, 3 and 4 in a 2:2:2:2 ratio in the presence of 1 eq. of Fe(BF₄)₂ and 1 eq. of Cu(BF₄) in CD₃CN (Figure 1). After 18 h at 60 °C, the ¹H NMR spectrum of the crude mixture (Figure 1), was not consistent with the complete self-sorting of the initial reagents into the expected complexes [Cu(1,4)₂]⁺ and [Fe(2,3)₂]²⁺, the notation (n,m) refers to the imine-based constituent generated by the condensation of amine n with aldehyde m (in no specific order). Three different sets of signals were observed. These could be assigned to the homoleptic complexes [Cu(1,4)₂]⁺ and [Fe(2,3)₂]²⁺ along with the heteroleptic complex [Fe(2,3)(2,4)]²⁺. The homo- and heteroleptic Fe(II) complexes formed in a 10:7 ratio. The homoleptic complex [Fe(2,4)₂]²⁺ containing two sterically hindered pyridine ligands 4 was not observed, attesting to its lower stability compared to the other two Fe(II) complexes.

Upon further heating of the reaction at 60 °C (see the Supporting Information), the ¹H NMR signals of [Fe(2,3)(2,4)]²⁺ started to fade. The disappearance of the heteroleptic complex was correlated with an increase in the population of [Cu(1,4)₂]⁺ and [Fe(2,3)₂]²⁺, hinting that the formation of [Fe(2,3)(2,4)]²⁺ is under kinetic control. However, after 20 days at 60 °C, [Fe(2,3)(2,4)]²⁺ was still present in the reaction mixture, thus under these conditions (60 °C, 20 days) this system is not under thermodynamic control, resulting in an incomplete self-sorting process. Thermodynamic control over the assembling of the system could be re-established by concentrating the reaction mixture. At 20 mM (up from 3.6 mM), [Fe(2,3)(2,4)]²⁺ was fully converted into [Cu(1,4)₂]⁺ and [Fe(2,3)₂]³⁺ after 20 days at 60 °C, the ¹H NMR spectrum of the reaction mixture being a superimposition of the spectra of the isolated complexes [Cu(1,4)₂]⁺ and [Fe(2,3)₂]³⁺.

To probe the driving forces governing the selective generation of [Cu(1,4)₂]⁺ and [Fe(2,3)₂]³⁺ at 20 mM, the formation of each one of the two complexes was attempted by mixing 1 eq. of the appropriate
metal salt with a 2:2:2:2 mixture of 1, 2, 3, 4 in CD$_3$CN at 60 °C (see the Supporting Information). The two reaction mixtures were monitored by $^1$H NMR spectroscopy over the course of 20 days.

Figure 1. Simultaneous generation of complexes [Cu(1,4)$_2$]$_2^+$ and [Fe(2,3)$_2$]$_2^{2+}$ through the self-sorting of their initial reactants. For clarity, the components 1 and 3 and the Cu(I) ions not incorporated in a complex have been omitted from the representation. Upper - Reaction conditions:

1:2:3:4:Cu(BF$_4$)$_2$:Fe(BF$_4$)$_2$ (2:2:2:2:1:1), 3.6 mM, CD$_3$CN, 60 °C, up to 20 days. Partial $^1$H NMR spectrum (400
Diagnostic signals of the free aldehydes 3 and 4 are highlighted by a green pentagon, two of the diagnostic signals of the free amine 1 are highlighted by grey squares.

When Fe(II) was added to the organic components, the affinity of Fe(II) for the imine ligand (2,3) was strong enough to ensure the exclusive formation of one Fe(II) complex after 18 h at 60 °C, [Fe(2,3)]^{2+} (see the Supporting Information). Whereas, when Cu(I) was added alone to the four organic components, [Cu(1,4)]^{+} did not form. Instead, an ill-defined Cu(I) complex was obtained (see the Supporting Information). This result shows that [Cu(1,4)]^{+} is not the thermodynamically most stable Cu(I) complex attainable from the initial library of components but instead constituent (1,4) is imposed upon Cu(I) by default via the ligand selection of Fe(II). Consequently, the formation of the thermodynamic product [Fe(2,3)]^{2+} is the main driving force of this self-sorting processes.

This system exemplifies how agonistic amplification between two constituents of a constitutional dynamic network can be exploited to force the expression of a product.\(^{11,8,9}\) It also confirms the validity of our initial design principles as, at a concentration of 20 mM, two fully non-identical metal complexes could be generated via the self-sorting of their initial components. However, it also exposed one major shortcoming of this strategy. At a lower concentration range (2.7 – 3.6 mM), the slower rearrangement of an intermediate generated under kinetic control trapped the system out-of-equilibrium—and thus out of a sorted outcome—for a length of time limiting the applicability of this type of systems. This shortcoming could be addressed by refining the design of the initial libray of components so that the rearrangement of this intermediate would be accelerated or its formation prevented.

b. Influence of the electronic parameters of the initial components on the fidelity of the self-sorting process

The influence of the electronic properties of the organic components on the output of their self-assembling in the presence of Fe(II) and Cu(I) was probed by modifying the electron-donating ability of the 4-substituent of aniline 1 or of the 6-substituent of the 2-formylpyridine 4.

The use of a more electron-rich aniline residue should generate a more stable Cu(I) complex\(^{15}\) and as complexes [Fe(2,3)(2,4)]^{2+} and [Cu(1,4)]^{+} share the same aldehyde component 4, the formation of a more stable Cu(I) complex may hamper the formation of [Fe(2,3)(2,4)]^{2+}. This hypothesis was tested by replacing the amine component 4 by the more electron rich N,N-dimethylaminoaniline 5 in the initial library of components (Figure 2).

When components 1, 3, 4, 5, Cu(BF\(_4\)) and Fe(BF\(_4\))\(_2\) were mixed in a 2:2:2:2:1:1 ratio in CD\(_3\)CN, the self-sorting of the system was clearly apparent in the \(^1\)H NMR spectrum of the crude mixture. After 3 days at 60 °C, only the diagnostic signals of the two homoleptic complexes [Fe(2,3)]^{2+} and [Cu(4,5)]^{+} were observed in the spectrum. The use of the electron rich aniline 5 did not inhibit the generation of the kinetic intermediate [Fe(2,3)(2,4)]^{2+}, as its slowly fading diagnostic signals were visible in the spectra of the reaction mixture after 18 h and 2 days, but 5 considerably enhanced the rate of the redistribution of the components of [Fe(2,3)(2,4)]^{2+} (see the Supporting Information).
Figure 2. Upper - Simultaneous generation of complexes $[\text{Cu}(\text{4,5})_2]^+$ and $[\text{Fe}(\text{2,3})_2]^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: $1:3:4:5:2:2:2:1:1$, CD$_3$CN, 60 °C, 18 h. Lower - Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 297 K) of the crude reaction mixture after 18 h at 60 °C, diagnostic signals of the complexes are colour coded, $[\text{Cu}(\text{4,5})_2]^+$ in red, $[\text{Fe}(\text{2,3})_2]^{2+}$ in purple, one of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle and one of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon.

Figure 3. Upper - Generation of complexes $[\text{Cu}(\text{1,6})_2]^+$ and $[\text{Fe}(\text{2,3})_2]^{2+}$ through the self-sorting of their initial reactants. For clarity, the components 1 and 6 and the Cu(I) ions not incorporated in a complex are omitted from the representation. Reaction conditions: $1:2:3:6:2:2:2:1:1$, CD$_3$CN, 60 °C, 18 h. Lower - Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 297 K) of the crude reaction mixture after 18 h at 60 °C, the diagnostic signals of the complexes are colour coded, $[\text{Cu}(\text{1,6})_2]^+$ in red and $[\text{Fe}(\text{2,3})_2]^{2+}$ in purple, one of the diagnostic signals of the free aldehyde 6 is highlighted by a grey circle and diagnostic signals of the free aniline 1 are highlighted by grey squares.
The formation of $[\text{Fe}(2,3)(2,4)]^{2+}$ could also be impeded by making the sterically hindered 2-formylpyridine 4 a poorer ligand. To do so, the methyl group of 4 was replaced with a slightly bigger and electron withdrawing CF$_3$ group (Figure 3). The addition of 1 eq. of Fe(BF$_4$)$_2$ and 1 eq. of Cu(BF$_4$) to a 2:2:2:2 mixture of components 1, 2, 3, 6 in CD$_3$CN prompted a rapid self-sorting of reaction mixture into complexes $[\text{Fe}(2,3)_2]^{2+}$ and $[\text{Cu}(1,6)]^{2+}$ after only 18 h at 60 °C (see Figure 3). The binding abilities of 6 were sufficiently weakened by the introduction of the CF$_3$ group so that any Fe(II) complex containing it was swiftly converted into $[\text{Fe}(2,3)_2]^{2+}$. However, the improvement of the rate of the self-sorting process came at the expense of the stability of the Cu(I) complex generated (see the Supporting Information).

c. Influence of the steric properties of the initial components on the self-sorting process

The influence of the steric hindrance borne by the organic components on the outcome of their self-assembling in the presence of Fe(II) and Cu(I) was investigated by modulating the bulkiness of the substituents ortho to the nitrogen atoms of the pyridine nucleus of aminoquinoline 2 and 2-formylpyridine 4. The incorporation of a phenyl ring in place of the methyl group of 2-formylpyridine 4 yielded the bulkier aldehyde 7 (Figure 4). In most cases, the enhanced steric congestion brought by the phenyl ring of 7 was sufficient to prevent the subsistence of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ at equilibrium.

When a 2:2:2:2 mixture of 2, 3, 7 and 8 in CD$_3$CN was treated with 1 eq. of Cu(BF$_4$) and 1 eq. of Fe(BF$_4$)$_2$, $[\text{Cu}(7,8)_2]^{2+}$ and $[\text{Fe}(2,3)_2]^{2+}$ were the only two complexes observable in the $^1$H NMR of the reaction mixture after 18 h at 60 °C (Figure 4). A similar result was obtained when aniline 5 was used in place of 8. During the monitoring of the organization of these two libraries at 60 °C by $^1$H NMR, both self-sorting processes were found to operate via the generation under kinetic control of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ (see the Supporting Information). However, the incorporation of a phenyl ring in place of the methyl group of 4 significantly increased the rate of rearrangement of the heteroleptic complex. Thermodynamic equilibrium was reached in only 18 h in the case of the library 2, 3, 5, 7 compared to 3 days in the case of the library 2, 3, 4, 5.

![Figure 4](image-url)  
*Figure 4.* Upper - Generation of complexes $[\text{Cu}(X,6)_2]^{2+}$ ($X = 1$ or 5 or 8) and $[\text{Fe}(2,3)_2]^{2+}$ through the self-sorting of their initial reactants. When amine 1 was used, trace amounts of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ were still observable even after 2 weeks at 60 °C. Reaction conditions: 1 or 5 or
When the electron poorer aniline 1 was used in place of 5 or 8, the heteroleptic complex [Fe(2,3)(2,7)]^{2+} was still observable in the reaction mixture after 2 weeks of heating at 60 °C (see the Supporting Information). By itself, the use the bulkier 2-formylpyridine 7 did not accelerate significantly the redistribution of the components of [Fe(2,3)(2,7)]^{2+} into [Cu(1,7)]^{+} and [Fe(2,3)]^{2+}. Even in the presence of 7, the assistance of a derivative of aniline more basic than 1 (such as 5 or 8) is required to obtain a time efficient self-sorting process.

The destabilization the Fe(II) heteroleptic complex needs not originate solely from the impairment of the binding abilities of a single one of its components. Instead, milder destabilizing features could be spread through several of its components, so that each one of these features would have a lesser effect on the binding abilities of the component bearing it, but the concurrent incorporation of several of these components in a single complex would be disfavored. If 6-methylpyridine 4 is reintroduced in the initial library of components in place of 7, the formation of [Fe(2,3)(2,4)]^{2+} could be hindered by introducing a methyl group ortho to the nitrogen atom of aminquinoline 2, such as in 9 (Figure 5).

An equimolar mixture of components 3, 4, 8 and 9 (2:2:2:2) was found to self-sort into the two homoleptic complexes [Cu(4,8)]^{+} and [Fe(3,9)]^{2+} after being treated with 1 eq. of Cu(BF_4) and 1 eq. of Fe(BF_4)_2 (Figure 5) in CD_3CN and left to react at 60 °C overnight. The ^1H NMR signals of the two complexes were the only ones visible in the spectrum of the crude reaction mixture after 18 h. Some of the ^1H NMR signals of [Fe(3,9)]^{2+} were strongly shifted downfield compared to those of [Fe(2,3)]^{2+}, indicating that [Fe(3,9)]^{2+} must adopt a more distorted octahedral coordination geometry due to the bulkier aminoquinoline 9.

**Figure 5.** Upper - Generation of complexes [Cu(4,8)]^{+} and [Fe(3,9)]^{2+} through the self-sorting of their initial reactants. Reaction conditions: 3:4:8:9:Cu(BF_4):Fe(BF_4)_2 (2:2:2:1:1), CD_3CN, 60 °C, 18 h. Lower -
Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 297 K) of the crude reaction mixture after 18 h at 60 °C. The diagnostic signals of the complexes are colour coded, [Cu(4,8)$_2$]$^+$ in red and [Fe(3,9)$_2$]$^{2+}$ in purple.

The incorporation of both the sterically demanding components aminoquinoline 9 and 2-formylpyridine 7 in the initial library markedly improved the rate of self-sorting process by preventing the generation of the heteroleptic complex [Fe(3,9)(7,9)]$^{2+}$.

Upon the treatment of a 2:2:2:2 mixture of 3, 7, 8 and 9 in CD$_3$CN with 1 eq. of Fe(II) and 1 eq. of Cu(I), the formation of the complexes [Fe(3,9)$_2$]$^{2+}$ and [Cu(7,8)$_2$]$^+$ was complete (in the sense that no further changes in the $^1$H NMR spectrum were detectable) after about 100 min of heating at 60 °C. In absence of the sterically demanding aminoquinoline 9 (see the Supporting Information) the formation of the homoleptic complexes [Fe(2,3)$_2$]$^{2+}$ and [Cu(7,8)$_2$]$^+$ from their components took more than 800 min in similar conditions. During the monitoring by $^1$H NMR of the self-sorting of [Fe(3,9)$_2$]$^{2+}$ and [Cu(7,8)$_2$]$^+$, the formation of the heteroleptic complex [Fe(3,9)(7,9)]$^{2+}$ was not observed. The greater steric hindrance of aminoquinoline 9 compared to 2 is likely to disfavor the inclusion of any other sterically congested components (such as 7) in a Fe(II) complex containing it. By preventing the generation of Fe(II) complexes other than [Fe(3,9)$_2$]$^{2+}$, 9 allows for a quick establishment of the thermodynamic equilibrium state of the system. Such influence of steric effects on the kinetics of a self-assembly process, allowing for quicker establishment of the thermodynamic equilibrium state, deserves further exploration in view of its interest for the design of complex dynamic systems.

d. Influence of the nature of the metal cation connectors on the self-sorting process

The influence of the coordination preferences of the metal cations triggering the self-sorting process on its fidelity was studied by altering the nature of, either the tetracoordinated metal cation used or the hexacoordinated one. We have shown earlier that a library composed of components 2, 3, 7 and 8 was able to self-sort into [Cu(7,8)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$ when treated with the appropriate metal salts (Figure 4). Now, the same library of components was treated with either a combination of Ag(I) and Fe(II) or a combination of Cu(I) and Zn(II).

The addition of 1 eq. Ag(I) and 1 eq. Fe(II) to a 2:2:2:2 mixture of 2, 3, 7 and 8 in CD$_3$CN resulted almost exclusively in the formation of the two expected homoleptic complexes [Ag(7,8)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$ after 18 h at 60°C. In the $^1$H NMR spectrum of the crude reaction mixture, only small traces of hydrolysis of the constituent (7,8) were observable besides the two complexes. Such an outcome corroborates our hypothesis that the formation of the octahedral complex is the main driving force of the self-sorting of the library. Thus, the nature of the tetracoordinated metal cation employed has little influence on the outcome of the self-sorting process and Ag(I) could be used in place of Cu(I).

Conversely, the substitution of Fe(II) for Zn(II) was found to have more dramatic effects on the output of the self-sorting process.
Figure 6. Upper - Generation of complexes $[\text{Ag}(7,8)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: $2:3:7:8:\text{Ag(BF}_4\text{)}_2:\text{Fe(BF}_4\text{)}_2 (2:2:2:1:1)$, CD$_3$CN, 60 °C, 18 h. Lower - Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 297 K) of the crude reaction mixture after 18 h at 60 °C. The diagnostic signals of the complexes are colour coded, $[\text{Ag}(7,8)_2]^+$ in orange and $[\text{Fe}(2,3)_2]^{2+}$ in purple, one of the diagnostic signals of the free aldehyde 7 is designated by a grey circle.

When 1 eq. of Zn(BF$_4$)$_2$ and 1 eq. of Cu(BF$_4$) were mixed with an equimolar mixture of 2, 3, 7 and 8 (2:2:2:2) in CD$_3$CN, $^1$H NMR spectroscopy showed the presence of several other products alongside the two expected complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(2,3)_2]^{2+}$ after 18 h at 60 °C. Further heating of the reaction mixture at 60°C for up to 5 days did not change this outcome (see the Supporting Information). The increased number of products might be due to the more flexible and accommodating coordination of d$^{10}$ Zn(II) compared to low-spin d$^8$ Fe(II). Thus, the disparities in steric and electronic properties of components 2, 3, 7 and 8 became insufficient to guide the self-organization process of the library towards the formation of only/predominantly $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(2,3)_2]^{2+}$. Substitution of the derivative of aminoquinoline 2 by the sterically bulkier aminoquinoline 9, largely restored the fidelity of the self-sorting process. When an equimolar mixture of 3, 7, 8 and 9 (2:2:2:2) was mixed in CD$_3$CN with 1 eq. of Zn(BF$_4$)$_2$ and 1 eq. of Cu(BF$_4$), the diagnostic signals of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(3,9)_2]^{2+}$ dominated the $^1$H NMR spectrum of the crude reaction mixture after 18 h at 60 °C. In this latter case, the improvement of the fidelity of the self-sorting process can be imputed to the greater steric hindrance of aminoquinoline 9 compared to 2. Indeed, when 1 eq. of Zn(II) was added to a 2:2:2 mixture of 2, 3, 7 (see the Supporting Information), all three Zn(II) complexes accessible form these components formed after 2 days at 60 °C, namely $[\text{Zn}(2,3)_2]^{2+}$, $[\text{Zn}(2,3)(2,7)]^{2+}$ and $[\text{Zn}(2,7)_2]^{2+}$. This outcome did not change upon further heating of the mixture at 60 °C for up to 6 days. In contrast, the addition of 1 eq. of Zn(II) to a 2:2:2 mixture of 3, 7, 9 yielded almost exclusively a single Zn(II) complex, $[\text{Zn}(3,9)_2]^{2+}$, after 2 days at 60 °C. The above systems highlight the correlation existing between the narrowness of the coordination preferences of the metal ions use to drive the self-assembly of a system and the amount of instructions required in the organic components of this system to guide it towards a specific outcome.
Figure 7. A) Upper - Attempted generation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(2,3)_2]^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: $2:3:7:8:\text{Cu(BF}_4)_2:Zn(\text{BF}_4)_2$ (2:2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Lower - Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 297 K) of the crude reaction mixture after 18 h at 60 °C, the diagnostic signals of the complexes are colour coded, $[\text{Cu}(7,8)_2]^+$ in red and $[\text{Zn}(2,3)_2]^{2+}$ in green, one of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle. B) Upper - Generation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(3,9)_2]^{2+}$ through the self-sorting of their initial reagents. Reaction conditions: $3:7:8:9:\text{Cu(BF}_4)_2:Zn(\text{BF}_4)_2$ (2:2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Lower - Partial $^1$H NMR spectrum (400 MHz, CD$_3$CN, 297 K) of the crude reaction mixture after 18 h at 60 °C, the diagnostic signals of the complexes are colour coded, $[\text{Cu}(7,8)_2]^+$ in red and $[\text{Zn}(3,9)_2]^{2+}$ in green.

Conclusions

The unique coordination preferences of tetrahedral and octahedral metal cations can be exploited to drive the self-sorting of two amine components and two 2-formylpyridine components into two fully non-identical metal complexes of imine ligands.

The fidelity of the self-sorting of the two metal complexes was determined by the capacity of the octahedral metal ion to select its pair of components from the initial pool of reactants, the ligand of the
weaker tetrahedral metal ions being dictated by the components discarded by the octahedral metal ions.

The present study stresses the pivotal role of the kinetic intermediates of the various processes involved in the generation of the thermodynamic products of metal ion-driven dynamic covalent systems in reaching a given self-sorted outcome. The concentration, the electronic properties and the steric properties of the initial components of the system were all found to be crucial parameters to manipulate for avoiding kinetic trapping during the sorting of the system. The present study also illustrates how modest alterations of the coordination and/or structural features guiding the self-assembly of the systems can tip the balance between a sorted and disordered final output.

We anticipate that the information gleaned from our investigation will facilitate the design and the manipulation of complex CDNs of molecules having a wide compositional and interactional diversity, an important step towards rivalling with the mastery of biological systems at organizing and exploiting dynamic networks of molecules.

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SUPPORTING INFORMATION

Self-sorting of two imine-based metal complexes: balancing kinetics and thermodynamics in constitutional dynamic networks

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1. General experimental section

1.1 General material

Unless stated otherwise, solvents and commercial reagents were used as received. Dry toluene was obtained by passing the solvent through an activated alumina on a Pure Solv solvent purification system. All reactions requiring anhydrous conditions were carried out in oven-dried glassware and all reactions requiring inert gas atmosphere were performed under nitrogen using standard Schlenk techniques. All reactions not performed in a NMR tubes were agitated using magnetic stirrer bars. Room temperature is taken as 293 K. Flash column chromatography was carried out using silica gel (Geduran Si60, 40-63 µm, Merck) using eluents as specified. TLC was performed on precoated silica gel plates (Merck TLC silica gel 60 F254 aluminium plates) and product spots were visualized under UV light ($\lambda_{\text{max}}$ = 280 nm or 365 nm) or by staining with KMnO$_4$. Celite® was obtained for Sigma-Aldrich and refers to diatomaceous earth. Brine refers to a saturated aqueous solution of NaCl. Ammonia in methanol was prepared by bubbling gaseous ammonia in methanol.

1.2 Characterization and analysis methods

NMR spectra were recorded on a Bruker Avance III 400 MHz, Bruker Avance III HD 400 MHz spectrometer or Bruker Avance Neo 500 MHz spectrometer. NMR spectra were digitally processed (phase and baseline corrections, integration, peak analysis) using MestReNova 10.0. Deuterated acetonitrile (CD$_3$CN) was obtained from Sigma-Aldrich and used without further purification. Deuterated chloroform (CDCl$_3$) was obtained from Sigma-Aldrich and was passed through a plug of sodium bicarbonate immediately before use to remove any acidic impurities. Chemical shifts are reported in parts per million (ppm) from low to high frequency using residual protonated solvent signals as reference (for $^1$H NMR spectra CDCl$_3$ = 7.26 ppm, CD$_3$CN = 1.94 ppm; for $^{13}$C NMR spectra CDCl$_3$ = 77.16 ppm, CD$_3$CN = 1.32 ppm). Coupling constants ($J$) are reported in hertz (Hz). The multiplicity of the 1H signals are indicated using the following standard abbreviations: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br = broad, ddd = doublet of double doublets. NMR signals are reported in terms of chemical shift (δ), multiplicity, coupling constants ($J$), relative integral, and assignment, in that order. All resonances are reported to the nearest 0.01 ppm. $^1$H and $^{13}$C NMR assignments were made using 2D-NMR methods (COSY, ROESY, TOCSY, HSQC, HMBC) and are unambiguous unless stated otherwise. High resolution ESI mass spectra were obtained in-house at the Institute of Science and Supramolecular Engineering (ISIS) by direct injection into a ThermoFisher Exactive Plus EMR Orbitrap mass spectrometer.

2. Synthesis

2.1 Synthesis of the ligands

2.1.1 Synthesis of aldehyde 7

7 was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.$^{[51]}$
2.1.2 Synthesis of imine constituent (1,4)

(1,4) was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.\\(^{52}\)

2.2 Synthesis of mononuclear metal complexes

2.2.1 General synthetic procedure

The general synthetic procedure for forming the mononuclear complexes is shown in Scheme S1.

Scheme S1. Synthesis of mononuclear complexes \([\text{M(L)}_2]^{n^+}\).

**General synthetic procedure:** CD\(_3\)CN solutions of the 2-formylpyridine containing component (100 µL of 320 mM, 32 µmol, 2 eq.) and of the amine containing component (100 µL of 320 mM, 32 µmol, 2 eq.) were combined. The resulting mixture was either treated with a CD\(_3\)CN solution of Fe(BF\(_4\))·6H\(_2\)O (100 µL of 160 mM, 16 µmol, 1 eq.) or a CD\(_3\)CN solution of [Cu(CH\(_3\)CN\(_4\))]\((BF_4)\) (100 µL of 160 mM, 16 µmol, 1 eq.) or a CD\(_3\)CN solution of [Zn(C\(_2\)H\(_6\)OS)\(_6\)]\((BF_4)\)\(_2\) (100 µL of 160 mM, 16 µmol, 1 eq.) and heated at 60 °C for 18 h. After cooling to room temperature, diisopropyl ether (~1 mL) was added. A fine suspension of material formed which was collected on Celite, washed with water, EtOH, diethylether. The resulting solid was dissolved in acetonitrile and concentrated under reduced pressure to give the desired complex. In all cases, the desired complex appeared pure by NMR spectroscopy.

2.2.2 Synthesis of Cu\(^1\) complex \([\text{Cu}(1,4)\(_2\)](BF_4)\)

\([\text{Cu}(1,4)\(_2\)](BF_4)\) was synthesized using the general procedure described in section 2.2.1.

\(^1\)H-NMR (500 MHz, CD\(_3\)CN): \(\delta\) (ppm) 9.11 (s, 2H, H\(^7\)), 8.06 (t, \(J = 7.7\) Hz, 2H, H\(^4\)), 7.89 (d, \(J = 7.6\) Hz, 2H, H\(^8\)), 7.61 (d, \(J = 7.8\) Hz, 2H, H\(^5\)), 7.38 (d, \(J = 8.0\) Hz, 2H, H\(^9\)), 7.17 (d, \(J = 8.0\) Hz, 2H, H\(^10\)), 2.31 (s, 6H, H\(^1\)), 2.30 (s, 6H, H\(^12\)).

\(^{13}\)C-NMR (125.8 MHz, CD\(_3\)CN): \(\delta\) (ppm) 159.19 (C\(^2\)), 158.44 (C\(^7\)), 151.50 (C\(^8\)), 145.35 (C\(^6\)), 140.61 (C\(^11\)), 139.47 (C\(^9\)), 131.07 (C\(^10\)), 129.16 (C\(^5\)), 126.48 (C\(^3\)), 123.18 (C\(^3\)), 25.11 (C\(^1\)), 20.99 (C\(^12\)).

HRMS (ESI\(^+\)): \(m/z\) calcd. for \([\text{Cu}(1,4)\(_2\)]^+\) 483.1604 found 483.1599.
**Synthesis of Fe$^{II}$ complex [Fe(2,3)$_2$](BF$_4$)$_2$**

The complex [Fe(2,3)$_2$](BF$_4$)$_2$ was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.$^{[53]}$
Figure S4. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Fe$^{II}$ complex [Fe(2,3)$_2$](BF$_4$)$_2$.

2.2.4 Synthesis of Fe$^{II}$ complex [Fe(2,4)$_2$](BF$_4$)$_2$

[Fe(2,4)$_2$](BF$_4$)$_2$ was synthesized using the general procedure described in section 2.2.1.

$^1$H-NMR (500 MHz, CD$_3$CN): $\delta$ (ppm) 12.33 (br s, 2H, H$^7$), 9.26 (d, $J = 7.7$ Hz, 2H, H$^9$), 8.70 (br s, 2H, H$^{15}$), 8.55 (d, $J = 7.6$ Hz, 2H, H$^5$), 8.29 (d, $J = 8.2$ Hz, 2H, H$^{11}$), 8.20 (t, $J = 8.0$ Hz, 2H, H$^{10}$), 8.14 (d, $J = 8.3$ Hz, 2H, H$^{13}$), 7.91 (t, $J = 7.7$ Hz, 2H, H$^4$), 7.49 (dd, $J = 8.2$, 4.9 Hz, 2H, H$^{14}$), 7.43 (d, $J = 7.8$ Hz, 2H, H$^3$), 2.06 (s, 6H).

$^{13}$C-NMR (125.8 MHz, CD$_3$CN): $\delta$ (ppm) 171.12 (C$^2$), 164.32 (C$^7$), 157.72 (C$^6$), 157.33 (C$^{15}$), 147.03 (C$^{16}$), 140.67 (C$^8$), 139.71 (C$^4$), 138.51 (C$^{13}$), 134.31 (C$^3$), 132.50 (C$^{11}$), 131.65 (C$^{5-12}$), 130.27 (C$^{10}$), 128.53 (C$^{14}$), 120.98 (C$^9$), 25.88 (C$^1$).

HRMS (ESI+): $m/z$ calcd. for [Fe(2,4)$_2$](BF$_4$)$^+$ 637.1598 found 637.1580.

Figure S5. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Fe$^{II}$ complex [Fe(2,4)$_2$](BF$_4$)$_2$.

Figure S6. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Fe$^{II}$ complex [Fe(2,4)$_2$](BF$_4$)$_2$. 
2.2.5 Synthesis of Fe$^{II}$ complex $[\text{Fe}(2,3)(2,4)]\{\text{BF}_4\}_2$

Scheme S2. Synthesis of the heteroleptic complex $[\text{Fe}(2,3)(2,4)]^{2+}$.

CD$_3$CN solutions of the 2-formylpyridines 3 (50 µL of 320 mM, 16 µmol, 1 eq.) and 4 (50 µL of 320 mM, 16 µmol, 1 eq.) and a CD$_3$CN solution of amine 2 (100 µL of 320 mM, 32 µmol, 2 eq.) were combined. The resulting mixture was treated with a CD$_3$CN solution of Fe(BF$_4$)$_2$ (100 µL of 160 mM, 16 µmol, 1 eq.) and was heated at 60 °C for 18 h. The complexes were not isolated, all the following analysis were done on the crude reaction mixture.

The heteroleptic complex $[\text{Fe}(2,3)(2,4)]^{2+}$ could not be isolated. However, its $^1$H and $^{13}$C NMR data could be determined by comparing the HMBC, HSQC, ROESY and COSY spectra of complexes $[\text{Fe}(2,3)_2]\{\text{BF}_4\}_2$ and $[\text{Fe}(2,4)_2]\{\text{BF}_4\}_2$ prepared in isolation with the spectra of the reaction mixture described above. Due to overlapping signals in the $^1$H NMR spectrum, the multiplicity of some of the peaks could not be determined with precision.

$^1$H-NMR (500 MHz, CD$_3$CN): δ (ppm) 10.89 (s, 1H, H$^7$B), 10.70 (s, 1H, H$^7$A), 9.20-9.15 (m, 2H, H$^9$A+9B), 8.29 (d, $J = 7.8$ Hz, 1H, H$^{1A+5B}$), 8.27 (1H, H$^{15}$), 8.26 (1H, H$^{13A+11A\text{ or }11B}$), 8.18 (1H, H$^{11A\text{ or }11B}$), 8.13 (1H, H$^{10A+11B}$), 8.09 (1H, H$^{10B}$), 7.84 (t, $J = 7.7$ Hz, 1H, H$^{16}$), 7.74 (d, $J = 7.8$ Hz, 1H, H$^{14}$), 7.76 (s, 1H, H$^{6A}$), 7.58 (dd, $J = 5.2$, 1.3 Hz, 1H, H$^{15B}$), 7.20 (dd, $J = 8.3$, 5.1 Hz, 1H, H$^{14A}$), 7.06 (dd, $J = 8.3$, 5.2 Hz, 1H, H$^{14B}$), 7.00 (d, $J = 7.8$, 1.1 Hz, 1H, H$^{1B}$), 2.09 (s, 3H, H$^1$A), 1.94 (s, 3H, H$^1$B).

$^{13}$C-NMR (125.8 MHz, CD$_3$CN): δ (ppm) 168.40 (C$^{2b}$), 166.62 (C$^{7b}$), 164.89 (C$^{7a}$), 159.78 (C$^{6b}$), 158.90 (C$^{15A}$), 158.86 (C$^{5a}$), 156.92 (C$^{15B}$), 155.55 (C$^{6a}$), 150.18 (C$^{16A}$), 149.30 (C$^{16B}$), 143.09 (C$^{6A}$), 142.61 (C$^{6B}$), 140.53 (C$^{2A}$), 139.68 (C$^{2A}$), 139.63 (C$^{4B}$), 138.15 (C$^{13A}$), 138.08 (C$^{13B}$), 131.93 (C$^{11A\text{ or }11B}$), 131.81 (C$^{10B}$), 130.82 (C$^{4A}$), 130.72 (C$^{12A\text{ or }12B}$), 130.07 (C$^{12A\text{ or }12B}$), 130.49 (C$^{11A\text{ or }11B}$), 129.92 (C$^{5b}$), 129.91 (C$^{10A}$), 129.88 (C$^{3b}$), 125.14 (C$^{14}$), 124.89 (C$^{14b}$), 119.71 (C$^{5a\text{ or }9b}$), 119.29 (C$^{5a\text{ or }9b}$), 24.31 (C$^{1B}$), 18.77 (C$^{1A}$).

As $[\text{Fe}(2,3)(2,4)]\{\text{BF}_4\}_2$, $[\text{Fe}(2,3)_2]\{\text{BF}_4\}_2$ and $[\text{Fe}(2,4)_2]\{\text{BF}_4\}_2$ have the same mass, the formation of $[\text{Fe}(2,3)(2,4)]\{\text{BF}_4\}_2$ could not be confirmed by mass spectrometry.
Figure S7. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (top) complex [Fe(2,3)$_2$]$^{2+}$, (middle) complex [Fe(2,4)$_2$]$^{2+}$, (bottom) the crude reaction mixture obtained by mixing 2, 3, 4 and Fe(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h. The diagnostic signals of the heteroleptic complex [Fe(2,3)(2,4)]$^{2+}$ are colored in orange and one of the diagnostic signals of the free aldehyde 4 is highlighted by a grey circle.

Figure S8. Partial HRESI-MS spectra of the reaction mixture obtained by mixing 2, 3, 4 and Fe(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.
Figure S9. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of the reaction mixture obtained by mixing 2, 3, 4 and Fe(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

Figure S10. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of the reaction mixture obtained by mixing 2, 3, 4 and Fe(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

2.2.6 Synthesis of Fe$^{II}$ complex [Fe(2,7)$_2$(BF$_4$)$_2$]

[Fe(2,7)$_2$(BF$_4$)$_2$] was synthesized using the general procedure described in section 2.2.1.

Due to the broadness of most peaks of [Fe(2,7)$_2$(BF$_4$)$_2$] (at 297 K or 243 K in CD$_3$CN) the $^1$H NMR and $^{13}$C NMR spectra of the complex could not be assigned with precision.

$^1$H-NMR (500 MHz, CD$_3$CN): $\delta$ (ppm) 14.96 (br s, 2H), 11.04 (br s, 2H), 10.62 (br s, 2H), 10.31 (br s, 2H), 9.84 (br s, 2H), 8.93 (br s, 2H), 8.84 (br s, 2H), 8.51 (d, $J = 7.6$ Hz, 2H), 8.04 (d, $J = 7.9$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.05 (br s, 4H), 6.54 (br s, 4H).

The chemical shift of two of the protons of [Fe(2,7)$_2$(BF$_4$)$_2$] could not be found.

$^{13}$C-NMR (125.8 MHz, 243 K, CD$_3$CN): $\delta$ (ppm) 194.79, 170.16, 161.83, 156.22, 140.78, 138.62, 138.09, 132.14, 131.68, 130.51, 129.68, 129.33, 128.82, 128.68, 127.65, 127.50, 125.50, 121.33, 120.64.

HRMS (ESI+): $m/z$ calcd. for [(Fe(2,7)$_2$(BF$_4$)$_2$]$^+$ 761.1913 found 761.1895.
**Figure S11.** $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Fe$^{II}$ complex $[\text{Fe}(2,7)_2](\text{BF}_4)_2$.

**Figure S12.** $^{13}$C NMR (125 MHz, 243 K, CD$_3$CN) of Fe$^{II}$ complex $[\text{Fe}(2,7)_2](\text{BF}_4)_2$.

### 2.2.7 Synthesis of Fe$^{II}$ complex $[\text{Fe}(2,3)(2,7)](\text{BF}_4)_2$

![Chemical structure](image)

Scheme S3. Synthesis of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$.

CD$_3$CN solutions of the 2-formylpyridines 3 (50 µL of 320 mM, 16 µmol, 1 eq.) and 7 (50 µL of 320 mM, 16 µmol, 1 eq.) and a CD$_3$CN solution of amine 2 (100 µL of 320 mM, 32 µmol, 2 eq.) were combined. The resulting mixture was treated with a CD$_3$CN solution of Fe(BF$_4$)$_2$ (100 µL of 160 mM, 16 µmol, 1 eq.) and was heated at 60 °C for 18 h. The complexes were not isolated, all the following analysis were done on the crude reaction mixture.
The heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ could not be isolated. However, its $^1H$ and $^{13}C$ NMR data could be determined by comparing the HMBC, HSQC, ROESY and COSY spectra of complexes $[\text{Fe}(2,3)](\text{BF}_4)_2$ and $[\text{Fe}(2,7)](\text{BF}_4)_2$ prepared in isolation with the spectra of the reaction mixture described above.

$^1H$-NMR (500 MHz, CD$_3$CN): $\delta$ (ppm) 11.04 (s, 1H, H$_{10B}$), 9.77 (s, 1H, H$_{7B}$), 9.20 (dd, $J = 6.8, 2.1$ Hz, 1H, H$_{12B}$), 8.49 (dd, $J = 7.8, 1.5$ Hz, 1H, H$_{8B}$), 8.39 (dd, $J = 7.8, 1.0$ Hz, 1H, H$_{10A}$), 8.27 (dd, $J = 5.2, 1.4$ Hz, 1H, H$_{15A}$), 8.23 (dd, $J = 8.3, 1.3$ Hz, 1H, H$_{16B}$), 8.14 (d, $J = 8.0$ Hz, 1H, H$_{14A}$), 8.10 (d, $J = 8.1$ Hz, 1H, H$_{11A}$), 8.09 (t, $J = 8.1$, 1H, H$_{12B}$), 8.09 (d, $J = 8.1$ Hz, 1H, H$_{11A}$), 8.05 (d, $J = 8.0$ Hz, 1H, H$_{10A}$), 7.78 (d, $J = 1.6$ Hz, 1H, H$_{16A}$), 7.76 (dd, $J = 8.0, 1.9$, 1H, H$_{16B}$), 7.52 (tt, $J = 7.6, 1.3$ Hz, 1H, H$_{18B}$), 7.37 (dd, $J = 5.2, 1.3$ Hz, 1H, H$_{16B}$), 7.34 (br s, 2H, H$_{2B}$ or 3B), 7.21 (dd, $J = 8.3, 5.1$ Hz, 1H, H$_{14A}$), 6.98 (dd, $J = 8.0$, 1H, H$_{17B}$), 6.71 (br s, 2H, H$_{2B}$ or 3B), 2.13 (s, 3H, H$_{1A}$).

$^{13}C$-NMR (125.8 MHz, CD$_3$CN): $\delta$ (ppm) 169.26 (C$_{5B}$), 166.12 (C$_{10B}$), 163.07 (C$_{7A}$), 159.65 (C$_{9B}$), 158.84 (C$_{5A}$), 158.25 (C$_{15A}$), 157.13 (C$_{18B}$), 155.57 (C$_{6A}$), 149.83 (C$_{16A}$), 149.33 (C$_{19B}$), 142.84 (C$_{6A}$), 142.76 (C$_{11B}$), 140.20 (C$_{2A}$), 139.76 (C$_{14A}$), 139.05 (C$_{7B}$), 138.39 (C$_{4B}$), 138.12 (C$_{16B}$), 137.99 (C$_{13A}$), 131.85 (C$_{14B}$), 131.75 (C$_{13B}$), 131.54 (C$_{11A}$), 130.60 (C$_{18}$), 130.53 (C$_{6B}$), 130.48 (C$_{16B}$), 130.44 (C$_{4A}$), 130.20 (C$_{12A}$), 129.34 (C$_{10A}$), 128.69 (C$_{2B}$ or 3B), 124.86 (C$_{14A}$), 124.82 (C$_{17B}$), 119.72 (C$_{6A}$), 119.25 (C$_{12B}$), 18.74 (C$_{1A}$).

HRMS (ESI+): m/z calcd. for $[(\text{Fe}(2,3)(2,7))(\text{BF}_4)]^+$ 699.1750 found 699.1737.

$\text{Fe}(2,7)]^2+\text{, (middle) complex }\text{Fe}(2,3)]^2+$, (bottom) the crude reaction mixture obtained by mixing 2, 3, 7 and Fe(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h. The diagnostic signals of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ are colored in orange.

Figure S13. Partial $^1H$ NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (top) complex $[\text{Fe}(2,7)]^{2+}$, (middle) complex $[\text{Fe}(2,3)]^{2+}$, (bottom) the crude reaction mixture obtained by mixing 2, 3, 7 and Fe(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h. The diagnostic signals of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ are colored in orange.
**Figure S14.** Partial HRESI-MS spectra of the reaction mixture obtained by mixing 2, 3, 7 and Fe(BF₄)₂ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

**Figure S15.** ¹H NMR (500 MHz, 297 K, CD₃CN) of the reaction mixture obtained by mixing 2, 3, 7 and Fe(BF₄)₂ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

**Figure S16.** ¹³C NMR (125 MHz, 297 K, CD₃CN) of the reaction mixture obtained by mixing 2, 3, 7 and Fe(BF₄)₂ in the molar ratio 2:1:1:1 at 60 °C for 18 h.
2.2.8  **Synthesis of Cu(I) complex [Cu(4,5)_2](BF_4)**

![Chemical Structure](image)

[Cu(4,5)_2](BF_4) was synthesized using the general procedure described in section 2.2.1.

**¹H-NMR (500 MHz, CD_3CN):** \(\delta\) (ppm) 9.02 (br s, 2H, H^7), 7.99 (t, \(J = 7.7\) Hz, 2H, H^4), 7.76 (br s, 2H, H^5), 7.52 (d, \(J = 7.7\) Hz, 2H, H^3), 7.46 (br s, 4H, H^6), 6.65 (d, \(J = 8.2\) Hz, 4H, H^10), 2.93 (br s, 12H, H^12), 2.25 (s, 6H, H^1).

**¹³C-NMR (125.8 MHz, CD_3CN):** \(\delta\) (ppm) 158.92 (C^2), 152.41 (C^6), 152.14 (C^7, C^11), 139.32 (C^4), 136.08 (C^8), 127.99 (C^3), 125.42 (C^5), 125.06 (C^9), 113.06 (C^10), 40.47 (C^12), 25.10 (C^1).

**HRMS (ESI+):** m/z calcld. for [Cu(4,5)_2]^+ 541.2135 found 541.2125.

**Figure S17.** ¹H NMR (500 MHz, 297 K, CD_3CN) of Cu(I) complex [Cu(4,5)_2](BF_4).

**Figure S18.** ¹³C NMR (125 MHz, 297 K, CD_3CN) of Cu(I) complex [Cu(4,5)_2](BF_4).

2.2.9  **Synthesis of Cu(I) complex [Cu(1,6)_2](BF_4)**

![Chemical Structure](image)

CD_3CN solutions of 1 (100 µL of 320 mM, 32 µmol, 2 eq.) and of 6 (100 µL of 320 mM, 32 µmol, 2 eq.) were combined. The resulting mixture was treated with a CD_3CN solution of [Cu(CH_3CN)_4](BF_4) (100 µL of 160 mM, 16 µmol, 1 eq.) and heated at 60 °C for 18 h. [Cu(1,6)_2](BF_4) was not stable enough to be isolated by precipitation, all the present experiments and analysis were done on the crude reaction mixture.
\(^1\)H-NMR (500 MHz, CD\(_3\)CN): \(\delta\) (ppm) 8.95 (s, 2H, H\(_7\)), 8.32 – 8.28 (m, 4H, H\(^{14}\)), 8.07 – 8.01 (m, 2H, H\(^{10}\)), 7.46 (d, \(J = 8.3\) Hz, 4H, H\(^{9}\)), 7.28 (d, \(J = 8.1\) Hz, 4H, H\(^{11}\)), 2.36 (s, 6H, H\(^{12}\)).

\(^1\)C-NMR (125.8 MHz, CD\(_3\)CN): \(\delta\) (ppm) 157.86 (C\(^7\)), 154.25 (C\(^6\)), 147.42 (q, \(J = 34.7\) Hz, C\(^2\)), 146.24 (C\(^8\)), 141.37 (C\(^4\)), 140.47 (C\(^11\)), 131.15 (C\(^10\)), 129.57 (C\(^5\)), 124.88 (C\(^3\)), 123.23 (C\(^9\)), 121.89 (C\(^1\)), 21.14 (C\(^12\)).

HRMS (ESI\(^+\)): \(m/z\) calcd. for [Cu(1,6)]\(^2\)+ 591.1039 found 591.1031.

**Figure S19.** \(^1\)H NMR (500 MHz, 297 K, CD\(_3\)CN) of Cu\(^1\) complex [Cu(1,6)]\(^2\)(BF\(_4\)).

**Figure S20.** \(^1\)C NMR (125 MHz, 297 K, CD\(_3\)CN) of Cu\(^1\) complex [Cu(1,6)]\(^2\)(BF\(_4\)).

2.2.10 **Synthesis of Cu\(^1\) complex [Cu(1,7)]\(^2\)(BF\(_4\))**

[Cu(1,7)]\(^2\)(BF\(_4\)) was synthesized using the general procedure described in section 2.2.1.

\(^1\)H-NMR (500 MHz, CD\(_3\)CN): \(\delta\) (ppm) 8.98 (s, 2H, H\(^7\)), 8.03 (t, \(J = 7.8\) Hz, 2H, H\(^7\)), 7.80 (dd, \(J = 7.7, 1.0\) Hz, 2H, H\(^8\)), 7.70 (dd, \(J = 7.9, 1.0\) Hz, 2H, H\(^8\)), 7.41 (d, \(J = 8.4\) Hz, 4H, H\(^{12}\)), 7.36 (d, \(J = 7.3\) Hz, 4H, H\(^3\)), 7.19 (d, \(J = 8.2\) Hz, 4H, H\(^{13}\)), 7.15 (d, \(J = 7.4\) Hz, 2H, H\(^9\)), 7.06 (t, \(J = 7.6\) Hz, 4H, H\(^3\)), 2.32 (s, 6H, H\(^{15}\)).

\(^1\)C-NMR (125.8 MHz, CD\(_3\)CN): \(\delta\) (ppm) 158.85 (C\(^5\)), 158.27 (C\(^10\)), 152.17 (C\(^9\)), 145.15 (C\(^11\)), 140.75 (C\(^14\)), 139.70 (C\(^4\)), 139.60 (C\(^7\)), 131.14 (C\(^13\)), 130.22 (C\(^2\)), 128.71 (C\(^3\)), 128.40 (C\(^3\)), 128.03 (C\(^6\)), 127.35 (C\(^3\)), 123.49 (C\(^12\)), 21.11 (C\(^15\)).

HRMS (ESI\(^+\)): \(m/z\) calcd. for [Cu(1,7)]\(^2\)+ 607.1917 found 607.1902.
Figure S21. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Cu complex [Cu(1,7)$_2$(BF$_4$)$_2$].

Figure S22. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Cu complex [Cu(1,7)$_2$(BF$_4$)$_2$].

2.2.11 Synthesis of Cu complex [Cu(5,7)$_2$(BF$_4$)$_2$]

[Cu(5,7)$_2$](BF$_4$)$_2$ was synthesized using the general procedure described in section 2.2.1.

$^1$H-NMR (500 MHz, CD$_3$CN): $\delta$ (ppm) 8.91 (s, 2H, H$_{10}$), 7.95 (t, J = 7.8 Hz, 2H, H$_1^1$), 7.68 (d, J = 7.4 Hz, 2H, H$_6^6$), 7.58 (d, J = 7.7 Hz, 2H, H$_6^9$), 7.51 (d, J = 9.1 Hz, 4H, H$_{12}^4$), 7.31 (d, J = 7.2 Hz, 4H, H$_8^8$), 7.12 (t, J = 7.3 Hz, 2H, H$_1^3$), 7.02 (t, J = 7.4 Hz, 4H, H$_2^2$), 6.65 (d, J = 9.1 Hz, 4H, H$_{13}^1$), 2.95 (s, 12H, H$_{15}^1$).

$^{13}$C-NMR (125.8 MHz, CD$_3$CN): $\delta$ (ppm) 158.57 (C$_5$), 152.96 (C$_9$), 152.42 (C$_{14}$), 151.88 (C$_{10}$), 139.90 (C$_4$), 139.20 (C$_7$), 135.73 (C$_{11}$), 129.94 (C$_1$), 128.53 (C$_2$), 128.33 (C$_3$), 126.82 (C$_6$), 126.32 (C$_8$), 125.27 (C$_{12}$), 113.01 (C$_{13}$), 40.46 (C$_{15}$).

HRMS (ESI$^+$): m/z calcld. for [Cu(5,7)$_2$]$^+$ 665.2448 found 665.2437.

Figure S23. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Cu complex [Cu(5,7)$_2$(BF$_4$)$_2$].
Figure S24. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Cu$^1$ complex [Cu(5,7)$_2$(BF$_4$)].

2.2.12 Synthesis of Cu$^1$ complex [Cu(7,8)$_2$(BF$_4$)]

[Cu(7,8)$_2$(BF$_4$)] was synthesized using the general procedure described in section 2.2.1.

$^1$H-NMR (500 MHz, CD$_3$CN): δ (ppm) 8.94 (s, 2H, H$_{10}$), 8.03 (t, J = 7.7 Hz, 2H, H$_7$), 7.79 (d, J = 7.6 Hz, 2H, H$_9$), 7.70 (d, J = 7.8 Hz, 2H, H$_8$), 7.50 (d, J = 9.0 Hz, 4H, H$_{12}$), 7.42 – 7.33 (m, 4H, H$_3$), 7.20 – 7.13 (m, 1H, H$_1$), 7.09 (t, J = 6.7 Hz, 4H, H$_2$), 6.90 (d, J = 9.0 Hz, 4H, H$_{13}$), 3.78 (s, 6H, H$_{15}$).

$^{13}$C-NMR (125.8 MHz, CD$_3$CN): δ (ppm) 161.54 (C$_{14}$), 158.83 (C$_5$), 156.49 (C$_{10}$), 152.38 (C$_9$), 140.49 (C$_4$), 139.78 (C$_{11}$), 139.57 (C$_7$), 130.20 (C$_1$), 128.73 (C$_2$), 128.43 (C$_{13}$), 127.74 (C$_6$), 127.04 (C$_8$), 125.20 (C$_{12}$), 115.63 (C$_{13}$), 56.32 (C$_{15}$).

HRMS (ESI+): m/z calcd. for [Cu(7,8)$_2$]$^+$ 639.1816 found 639.1813.

Figure S25. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Cu$^1$ complex [Cu(7,8)$_2$(BF$_4$)].

Figure S26. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Cu$^1$ complex [Cu(7,8)$_2$(BF$_4$)].
2.2.13 **Synthesis of Cu\textsuperscript{I} complex [Cu(4,8)\textsubscript{2}](BF\textsubscript{4})**

[Cu(4,8)\textsubscript{2}](BF\textsubscript{4}) was synthesized using the general procedure described in section 2.2.1.

\textsuperscript{1}H-NMR (500 MHz, CD\textsubscript{3}CN): \(\delta\) (ppm) 9.09 (s, 2H, H\textsubscript{7}), 8.05 (t, \(J = 7.7\) Hz, 2H, H\textsubscript{4}), 7.87 (d, \(J = 7.6\) Hz, 2H, H\textsubscript{5}), 7.59 (d, \(J = 7.8\) Hz, 2H, H\textsubscript{3}), 7.48 (d, \(J = 8.9\) Hz, 4H, H\textsubscript{9}), 6.89 (d, \(J = 9.0\) Hz, 4H, H\textsubscript{10}), 3.76 (s, 6H, H\textsubscript{12}), 2.29 (s, 6H, H\textsubscript{1}).

\textsuperscript{13}C-NMR (125.8 MHz, CD\textsubscript{3}CN): \(\delta\) (ppm) 161.52 (C\textsubscript{11}), 159.20 (C\textsubscript{2}), 156.74 (C\textsubscript{7}), 151.82 (C\textsubscript{6}), 140.74 (C\textsubscript{8}), 139.52 (C\textsubscript{4}), 128.95 (C\textsubscript{3}), 126.30 (C\textsubscript{5}), 125.00 (C\textsubscript{9}), 115.69 (C\textsubscript{10}), 56.29 (C\textsubscript{12}), 25.17 (C\textsubscript{1}).

HRMS (ESI\textsuperscript{+}): \(m/z\) calcd. for [Cu(4,8)\textsubscript{2}]\textsuperscript{+} 515.1503 found 515.1496.

![Figure S27. \textsuperscript{1}H NMR (500 MHz, 297 K, CD\textsubscript{3}CN) of Cu\textsuperscript{I} complex [Cu(4,8)\textsubscript{2}](BF\textsubscript{4}).](image)

2.2.14 **Synthesis of Fe\textsuperscript{II} complex [Fe(3,9)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}**

[Fe(3,9)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} was synthesized using the general procedure described in section 2.2.1.

\textsuperscript{1}H-NMR (500 MHz, 275 K, CD\textsubscript{3}CN): \(\delta\) (ppm) 12.55 (br s, 2H, H\textsubscript{7}), 9.38 (d, \(J = 7.7\) Hz, 2H, H\textsubscript{5}), 8.76 (br s, 2H, H\textsubscript{3}), 8.44 (d, \(J = 7.2\) Hz, 2H, H\textsubscript{11}), 8.43 (d, \(J = 6.6\) Hz, 2H, H\textsubscript{4}), 8.29 (t, \(J = 7.8\) Hz, 2H, H\textsubscript{10}), 8.19 (d, \(J = 8.3\) Hz, 2H, H\textsubscript{13}), 7.76 (d, \(J = 7.8\) Hz, 2H, H\textsubscript{3}), 7.50 (d, \(J = 8.1\) Hz, 2H, H\textsubscript{14}), 2.12 (s, 6H, H\textsubscript{1}), 1.99 (s, 6H, H\textsubscript{1}).
\(^{13}\)C-NMR (125.8 MHz, 275 K, CD\(_3\)CN): \(\delta\) (ppm) 175.67 (C\(^{15}\)), 160.04 (C\(^7\)), 154.16 (C\(^6\)), 152.89 (C\(^5\)), 148.23 (C\(^17\)), 145.65 (C\(^2\)), 142.41 (C\(^8\)), 139.24 (C\(^{13}\)), 138.40 (C\(^3\)), 133.18 (C\(^4\)), 132.72 (C\(^{11}\)), 131.72 (C\(^{14}\)), 130.67 (C\(^{12}\)), 129.35 (C\(^{10}\)), 121.85 (C\(^9\)), 27.33 (C\(^{16}\)), 19.36 (C\(^1\)).

HRMS (ESI\(^+\)): m/z calcd. for [Fe(3,9)\(_2\)]\(^{2+}\) 289.0935 found 289.0933.

**Figure S29.** \(^1\)H NMR (500 MHz, 275 K, CD\(_3\)CN) of Fe\(^{II}\) complex [Fe(3,9)\(_2\)](BF\(_4\))\(_2\).

**Figure S30.** \(^{13}\)C NMR (125 MHz, 275 K, CD\(_3\)CN) of Cu\(^{I}\) complex [Fe(3,9)\(_2\)](BF\(_4\))\(_2\).
Figure S31. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN) of the Fe$^{II}$ complex [Fe(3,9)$_2$(BF$_4$)$_2$] at variable temperature from 303 K to 243 K. VT-NMR was performed from high to low temperature, starting from 303 K. The position of the peak of H$^7$ is highlighted by grey circles and the position of the peak of H$^6$ is highlighted by green pentagons.

2.2.15 Synthesis of Ag$^+$ complex [Ag(7,8)$_2$(BF$_4$)$_2$]

[Ag(7,8)$_2$(BF$_4$)$_2$] was synthesized using the general procedure described in section 2.2.1.

$^1$H-NMR (500 MHz, CD$_3$CN): δ (ppm) 8.86 (s, 2H, H$^{10}$), 8.09 (t, J = 7.8 Hz, 2H, H$^7$), 7.79 (d, J = 7.9 Hz, 2H, H$^6$), 7.78 (d, J = 7.6 Hz, 2H, H$^8$), 7.56 (d, J = 7.3 Hz, 4H, H$^3$), 7.48 (d, J = 8.9 Hz, 4H, H$^{12}$), 7.20 (t, J = 7.4 Hz, 2H, H$^5$), 7.09 (t, J = 7.6 Hz, 4H, H$^2$), 6.95 (d, J = 8.9 Hz, 4H, H$^{11}$), 3.80 (s, 6H, H$^{15}$).

$^{13}$C-NMR (125 MHz, CD$_3$CN): δ (ppm) 161.34 (C$^{14}$), 159.67 (C$^5$), 157.49 (C$^{10}$), 150.70 (C$^9$), 141.16 (C$^{11}$), 140.78 (C$^8$), 140.66 (C$^7$), 130.53 (C$^3$), 129.34 (C$^2$), 128.10 (C$^{12}$), 127.18 (C$^6$), 125.18 (C$^{13}$), 115.70 (C$^{15}$), 56.34 (C$^{15}$).

HRMS (ESI+): m/z calcd. for [Ag(7,8)$_2$]$^+$ 683.1571 found 683.1572.

Figure S32. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Ag$^+$ complex [Ag(7,8)$_2$(BF$_4$)$_2$].

Figure S33. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Ag$^+$ complex [Ag(7,8)$_2$(BF$_4$)$_2$].
2.2.16 Synthesis of Zn\textsuperscript{II} complex [Zn(2,3)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}

[Zn(2,3)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} was synthesized using the general procedure described in section 2.2.1.

\textsuperscript{1}H-NMR (500 MHz, CD\textsubscript{3}CN): \(\delta\) (ppm) 9.84 (s, 2H, H\textsubscript{7}), 8.68 (d, \(J = 7.7\) Hz, 2H, H\textsubscript{5}), 8.54 (d, \(J = 8.3\) Hz, 2H, H\textsubscript{15}), 8.30 (d, \(J = 4.6\) Hz, 2H, H\textsubscript{13}), 8.24 (d, \(J = 8.3\) Hz, 2H, H\textsubscript{11}), 8.13 (d, \(J = 8.3\) Hz, 2H, H\textsubscript{1}), 8.05 (t, \(J = 8.0\) Hz, 2H, H\textsubscript{10}), 7.97 (s, 2H, H\textsubscript{6}), 7.96 (d, \(J = 7.4\) Hz, 2H, H\textsubscript{3}), 7.45 (dd, \(J = 8.3, 4.6\) Hz, 2H, H\textsubscript{14}), 2.18 (s, 6H, H\textsubscript{1}).

\textsuperscript{13}C-NMR (125.8 MHz, CD\textsubscript{3}CN): \(\delta\) (ppm) 158.22 (C\textsubscript{7}), 150.69 (C\textsubscript{6+15}), 145.36 (C\textsubscript{5}), 142.41 (C\textsubscript{2}), 142.14 (C\textsubscript{3}), 141.29 (C\textsubscript{16}), 140.98 (C\textsubscript{13}), 136.19 (C\textsubscript{8}), 131.80 (C\textsubscript{11}), 130.57 (C\textsubscript{12}), 130.21 (C\textsubscript{4}), 129.16 (C\textsubscript{10}), 124.34 (C\textsubscript{14}), 120.24 (C\textsubscript{9}), 18.59 (C\textsubscript{1}).

HRMS (ESI\textsuperscript{+}): \(m/z\) calcd. for [Zn(2,3)\textsubscript{2}]\textsuperscript{2+} 279.0750 found 279.0750.

![Figure S34](image1.png)

Figure S34. \textsuperscript{1}H NMR (500 MHz, 297 K, CD\textsubscript{3}CN) of Zn\textsuperscript{II} complex [Zn(2,3)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}.

![Figure S35](image2.png)

Figure S35. \textsuperscript{13}C NMR (125 MHz, 297 K, CD\textsubscript{3}CN) of Zn\textsuperscript{II} complex [Zn(2,3)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}.

2.2.17 Synthesis of Zn\textsuperscript{II} complex [Zn(2,7)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}

[Zn(2,7)\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} was synthesized using the general procedure described in section 2.2.1.
**1H-NMR (500 MHz, CD3CN):** δ (ppm) 9.07 (s, 2H, H10), 8.48 (dd, J = 8.4, 1.4 Hz, 2H, H18), 8.33 (dd, J = 7.8, 1.1 Hz, 2H, H12), 8.30 (dd, J = 4.7, 1.5 Hz, 2H, H16), 8.23 (t, J = 7.7 Hz, 2H, H7), 8.20 (dd, J = 8.4, 1 Hz, 2H, H14), 7.97 (t, J = 8.0 Hz, 2H, H13), 7.97 (dd, J = 7.6, 1.1 Hz, 2H, H6), 7.57 (dd, J = 7.8, 1.1 Hz, 2H, H6), 7.42 (dd, J = 8.2, 4.7 Hz, 2H, H17), 7.39 (tt, J = 7.6, 1.2 Hz, 2H, H17), 6.79 (t, J = 7.8 Hz, 4H, H2), 6.39 (dd, J = 8.1, 1.2 Hz, 4H, H3).

**13C-NMR (125.8 MHz, CD3CN):** δ (ppm) 162.13 (C5), 156.91 (C10), 150.43 (C18), 148.08 (C9), 142.28 (C7), 140.98 (C16), 140.40 (C19), 139.29 (C4), 135.49 (C11), 132.07 (C14), 131.28 (C6), 130.76 (C1), 130.44 (C15), 130.34 (C8), 129.38 (C2), 129.03 (C13), 128.58 (C3), 124.34 (C17), 120.58 (C12).

**HRMS (ESI+):** m/z calcd. for [Zn(2,7)]2⁺ 341.0906 found 341.0903.

**Figure S36.** 1H NMR (500 MHz, 297 K, CD3CN) of ZnII complex [Zn(2,7)]2(BF4)2.

**Figure S37.** 13C NMR (125 MHz, 297 K, CD3CN) of ZnII complex [Zn(2,7)]2(BF4)2.

**2.2.18 Synthesis of ZnII complex [Zn(2,3)(2,7)](BF4)2**

[Image: synthetic_diagram.png]

**[Zn(2,3)(2,7)](BF4)2**
CD₃CN solutions of the 2-formylpyridines 3 (50 µL of 320 mM, 16 µmol, 1 eq.) and 7 (50 µL of 320 mM, 16 µmol, 1 eq.) and a CD₃CN solution of amine 2 (100 µL of 320 mM, 32 µmol, 2 eq.) were combined. The resulting mixture was treated with a CD₃CN solution of [Zn(C₂H₆OS)₆](BF₄)₂ (100 µL of 160 mM, 16 µmol, 1 eq.) and was heated at 60 °C for 18 h. The complexes were not isolated, all the following experiments and analysis were done on the crude reaction mixture.

The heteroleptic complex [Zn(2,3)(2,7)]^{2+} could not be isolated. However, its ¹H and ¹³C NMR data could be determined by comparing the HMBC, HSQC, ROESY and COSY spectra of complexes [Zn(2,3)](BF₄)₂ and [Zn(2,7)](BF₄)₂ prepared in isolation with the spectra of the reaction mixture described above. Due to overlapping signals in the ¹H NMR spectrum, the multiplicity of some of the peaks could not be determined with precision.

**¹H-NMR (500 MHz, CD₃CN):** δ (ppm) 10.02 (s, 1H, H₇A), 9.06 (s, 1H, H₁₀B), 8.71 (d, J = 6.8 Hz, 1H, H₉A), 8.55 (dd, J = 6.1, 1.7 Hz, 2H, H₁₃A), 8.42 (dd, J = 6.0, 1.4 Hz, 1H, H₁₄B), 8.40 (2H, H₄A+₁₅A), 8.30 (t, J = 8.4 Hz, 1H, H₃A+₇B), 8.22 (d, J = 6.8 Hz, 1H, H₁₂B), 8.16 (d, J = 8.4 Hz, 1H, H₁₁A), 8.03 (d, J = 4.7, 1.4 Hz, 1H, H₁₈B), 8.02 (s, 1H, H₆A), 8.00 (d, J = 7.8 Hz, 1H, H₁₀A), 7.95 (d, J = 9.0 Hz, 1H, H₁₄B), 7.94 (d, J = 7.9 Hz, 1H, H₁₈B), 7.55 (dd, J = 7.8, 1.1 Hz, 1H, H₆B), 7.50 (dd, J = 8.3, 4.7 Hz, 1H, H₁₆A), 7.40 (d, J = 7.4 Hz, 1H, H₁₁B), 7.32 (dd, J = 8.3, 4.7 Hz, 1H, H₁₇B), 7.24 (tt, J = 7.4, 1.2 Hz, 1H, H₁₈B), 6.68 (t, J = 7.8 Hz, 2H, H₂B), 6.24 (dd, J = 8.0, 1.1 Hz, 2H, H₃B), 2.22 (s, 3H, H₁₄A).

**¹³C-NMR (125.8 MHz, CD₃CN):** δ (ppm) 162.44 (C₅B), 160.08 (C₇A), 155.15 (C₁₀B), 150.65 (C₁₅A), 150.63 (C₆A), 150.07 (C₁₈B), 148.34 (C₅A), 145.04 (C₁₈B), 144.97 (C₂A), 142.29 (C₃A+₇B), 141.14 (C₁₃A), 141.04 (C₁₈A), 140.97 (C₁₉B), 140.67 (C₁₆B), 139.34 (C₄B), 136.44 (C₈A), 135.35 (C₁₁B), 131.94 (C₁₁A), 131.26 (C₆B), 130.54 (C₁₃B), 130.40 (C₁₈B), 130.26 (C₁₅B), 130.18 (C₆A), 130.17 (C₁₄B), 129.10 (C₁₃B), 129.00 (C₈B), 128.99 (C₂B), 128.98 (C₁₉A), 128.19 (C₃B), 124.33 (C₁₄A), 124.17 (C₁₇B), 120.38 (C₁₂B), 120.29 (C₈A) 18.04 (C₁₄A).

**HRMS (ESI+):** m/z calcd. for [Zn(2,3)(2,7)]^{2+} 310.5843 found 310.5833.
**Figure S38.** Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (top) complex [Zn(2,3)$_2$]$^{2+}$, (middle) complex [Zn(2,7)$_2$]$^{2+}$, (bottom) the crude reaction mixture obtained by mixing 2, 3, 7 and Zn(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h. The diagnostic signals of the heteroleptic complex [Zn(2,3)(2,7)]$^{2+}$ are colored in orange.

**Figure S39.** Partial HRESI-MS spectra of the reaction mixture obtained by mixing 2, 3, 7 and Zn(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.
Figure S40. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of the reaction mixture obtained by mixing 2, 3, 7 and Zn(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

Figure S41. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of the reaction mixture obtained by mixing 2, 3, 7 and Zn(BF$_4$)$_2$, in the molar ratio 2:1:1:1 at 60 °C for 18 h.

2.2.19 Synthesis of Zn$^{II}$ complex [Zn(3,9)$_2$](BF$_4$)$_2$

[Zn(3,9)$_2$](BF$_4$)$_2$ was synthesized using the general procedure described in section 2.2.1.

$^1$H-NMR (500 MHz, CD$_3$CN): δ (ppm) 9.73 (s, 2H, H$_7$), 8.69 (d, $J = 7.8$ Hz, 2H, H$_8$), 8.52 (d, $J = 8.4$ Hz, 2H, H$_{13}$), 8.29 (d, $J = 8.2$ Hz, 2H, H$_{11}$), 8.09 – 7.99 (m, 4H, H$_{4-10}$), 7.87 (d, $J = 7.8$ Hz, 2H, H$_6$), 7.65 (s, 2H, H$_6$), 7.47 (d, $J = 8.4$ Hz, 2H, H$_{14}$), 2.12 (s, 6H, H$_1$), 2.07 (s, 6H, H$_{16}$).

$^{13}$C-NMR (125.8 MHz, CD$_3$CN): δ (ppm) 163.18 (C$_{15}$), 157.61 (C$_7$), 150.24 (C$_8$), 144.96 (C$_5$), 142.45 (C$_2$), 141.91 (C$_3$), 141.23 (C$_{13-17}$), 134.96 (C$_6$), 132.21 (C$_{11}$), 130.41 (C$_4$), 129.27 (C$_{12}$), 128.36 (C$_{10}$), 126.34 (C$_{14}$), 120.73 (C$_9$), 24.76 (C$_{16}$), 18.72 (C$_1$).

HRMS (ESI+): m/z calcd. for [Zn(3,9)$_2$](BF$_4$)$^+$ 673.1853 found 673.1821.
Figure S42. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Zn$^{II}$ complex [Zn(3,9)$_2$](BF$_4$)$_2$.

Figure S43. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Zn$^{II}$ complex [Zn(3,9)$_2$](BF$_4$)$_2$.

2.2.20 Synthesis of Zn$^{II}$ complex [Zn(7,9)$_2$](BF$_4$)$_2$

[Zn(7,9)$_2$](BF$_4$)$_2$ was synthesized using the general procedure described in section 2.2.1.

$^1$H-NMR (500 MHz, CD$_3$CN): $\delta$ (ppm) 8.77 (s, 2H, H$_{10}$), 8.52 (d, $J$ = 8.4 Hz, 2H, H$_{16}$), 8.21 (dd, $J$ = 8.4, 1.2 Hz, 2H, H$_{14}$), 8.05 (t, $J$ = 7.7 Hz, 2H, H$_1$), 7.98 (dd, $J$ = 7.6, 1.2 Hz, 2H, H$_8$), 7.91 (dd, $J$ = 7.8, 1.2 Hz, 2H, H$_{12}$), 7.77 (t, $J$ = 8.0 Hz, 2H, H$_{13}$), 7.54 (dd, $J$ = 7.8, 1.2 Hz, 2H, H$_9$), 7.49 (d, $J$ = 8.4 Hz, 2H, H$_{17}$), 6.97 (tt, $J$ = 7.5, 1.3 Hz, 2H, H$_5$), 6.78 (dt, $J$ = 6.9, 1.3 Hz, 4H, H$_3$), 6.62 (t, $J$ = 7.4 Hz, 4H, H$_2$), 2.10 (s, 6H, H$_{19}$).

$^{13}$C-NMR (125.8 MHz, CD$_3$CN): $\delta$ (ppm) 163.30 (C$_{18}$), 162.13 (C$_5$), 161.02 (C$_{10}$), 148.48 (C$_9$), 141.49 (C$_7$ or 16), 141.46 (C$_7$ or 16), 141.07 (C$_{20}$), 138.42 (C$_4$), 136.41 (C$_{12}$), 131.98 (C$_{14}$), 131.06 (C$_6$), 130.56 (C$_i$), 130.30 (C$_8$), 129.03 (C$_1$), 128.76 (C$_{15}$), 128.57 (C$_3$), 128.17 (C$_{13}$), 126.62 (C$_{17}$), 120.73 (C$_{12}$), 24.80 (C$_{19}$).

HRMS (ESI+): m/z calcd. for [Zn(7,9)$_2$]$^{2+}$ 355.1063 found 355.1059.
Figure S44. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of Zn$^{II}$ complex [Zn(7,9)$_2$(BF$_4$)$_2$].

Figure S45. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of Zn$^{II}$ complex [Zn(7,9)$_2$(BF$_4$)$_2$].

2.2.21 Synthesis of Zn$^{II}$ complex [Zn(3,9)(7,9)](BF$_4$)$_2$

Scheme S5. Synthesis of the heteroleptic complex [Zn(3,9)(7,9)]$^{2+}$.

CD$_3$CN solutions of the 2-formylpyridines 3 (50 µL of 320 mM, 16 µmol, 1 eq.) and 7 (50 µL of 320 mM, 16 µmol, 1 eq.) and a CD$_3$CN solution of amine 9 (100 µL of 320 mM, 32 µmol, 2 eq.) were combined. The resulting mixture was treated with a CD$_3$CN solution of [Zn(C$_2$H$_6$OS)$_6$](BF$_4$)$_2$ (100 µL of 160 mM, 16 µmol, 1 eq.) and was heated at 60 ºC for 18 h. The complexes were not isolated, all the following experiments and analysis were done on the crude reaction mixture.
The heteroleptic complex [Zn(3,9)(7,9)]^{2+} could not be isolated. However, its \(^1H\) and \(^{13}C\) NMR data could be determined by comparing the HMBC, HSQC, ROESY and COSY spectra of complexes [Zn(3,9)]\textsubscript{2}([BF\textsubscript{4}])\textsubscript{2} and [Zn(7,9)]\textsubscript{2}([BF\textsubscript{4}])\textsubscript{2} prepared in isolation with the spectra of the reaction mixture described above. Due to overlapping signals in the \(^1H\) NMR spectrum, the multiplicity of some of the peaks could not be determined with precision.

\(^1H\)-NMR (500 MHz, CD\textsubscript{2}CN): \(\delta\) (ppm) 9.91 (s, 1H, H\textsuperscript{7A}), 9.03 (s, 1H, H\textsuperscript{10B}), 8.72 (dd, \(J = 7.9, 1.2\) Hz, 1H, H\textsuperscript{1A}), 8.50 (d, \(J = 8.4\) Hz, 1H, H\textsuperscript{16B}), 8.44 (d, \(J = 8.4\) Hz, 1H, H\textsuperscript{13B}), 8.25 (dd, \(J = 8.4, 1.2\) Hz, 1H, H\textsuperscript{11A}), 8.21 (d, \(J = 7.4\) Hz, 1H, H\textsuperscript{16A}), 8.16 (dd, \(J = 8.4, 1.1\) Hz, 1H, H\textsuperscript{14B}), 8.11 (t, \(J = 7.7\) Hz, 1H, H\textsuperscript{17B}), 8.02 (1H, H\textsuperscript{10A}), 7.97 (d, \(J = 8.0\) Hz, 1H, H\textsuperscript{14B}), 7.91 (d, \(J = 7.7\) Hz, 1H, H\textsuperscript{12B}), 7.90 (ddd, \(J = 7.8, 2.0, 0.9\) Hz, 1H, H\textsuperscript{2A}), 7.82 (dd, \(J = 1.9, 0.7\) Hz, 1H, H\textsuperscript{6B}), 7.72 (t, \(J = 8.0\) Hz, 1H, H\textsuperscript{13B}), 7.51 (d, \(J = 8.3\) Hz, 1H, H\textsuperscript{17B}), 7.43 (ddd, \(J = 7.8, 1.1\) Hz, 1H, H\textsuperscript{6B}), 7.35 (d, \(J = 8.4\) Hz, 1H, H\textsuperscript{9A}), 7.02 (tt, \(J = 7.6, 1.3\) Hz, 1H, H\textsuperscript{1B}), 6.70 (t, \(J = 7.8\) Hz, 2H, H\textsuperscript{2B}), 6.48 (dd, \(J = 8.2, 1.3\) Hz, 2H, H\textsuperscript{1B}), 2.23 (s, 3H, H\textsuperscript{19B}), 2.19 (s, 3H, H\textsuperscript{1A}), 1.80 (s, 3H, H\textsuperscript{16A}).

\(^{13}C\)-NMR (125.8 MHz, CD\textsubscript{2}CN): \(\delta\) (ppm) 163.37 (C\textsuperscript{15A}), 163.15 (C\textsuperscript{18B}), 162.86 (C\textsuperscript{1B}), 161.11 (C\textsuperscript{7A}), 157.11 (C\textsuperscript{10A}), 121.09 (C\textsuperscript{9A}), 149.96 (C\textsuperscript{6A}), 148.55 (C\textsuperscript{19B}+5A), 144.64 (C\textsuperscript{2A}), 142.00 (C\textsuperscript{5A}), 141.37 (C\textsuperscript{18B}), 141.32 (C\textsuperscript{17A}), 141.30 (C\textsuperscript{20B}), 141.27 (C\textsuperscript{7B}), 141.02 (C\textsuperscript{13A}), 138.71 (C\textsuperscript{4B}), 136.25 (C\textsuperscript{8A}), 134.55 (C\textsuperscript{11B}), 132.29 (C\textsuperscript{11A}), 131.85 (C\textsuperscript{14B}), 131.70 (C\textsuperscript{6B}), 130.60 (C\textsuperscript{15B}), 130.57 (C\textsuperscript{12B}), 130.48 (C\textsuperscript{6A}), 130.30 (C\textsuperscript{2B}), 129.13 (C\textsuperscript{12A}), 128.69 (C\textsuperscript{15B}), 128.62 (C\textsuperscript{2B}), 128.31 (C\textsuperscript{10A}), 128.17 (C\textsuperscript{3B}), 127.99 (C\textsuperscript{13B}), 126.50 (C\textsuperscript{14A}), 126.33 (C\textsuperscript{17B}), 24.94 (C\textsuperscript{19B}), 24.50 (C\textsuperscript{16A}), 18.78 (C\textsuperscript{1A}).

HRMS (ESI+): m/z calcd. for [Zn(3,9)(7,9)]\textsuperscript{2+} 324.0984 found 324.0976.

**Figure S46.** Partial \(^1H\) NMR spectra (500 MHz, CD\textsubscript{2}CN, 297 K) of: (top) complex [Zn(2,3)]\textsubscript{2}\textsuperscript{2+}, (middle) complex [Zn(2,7)]\textsubscript{2}\textsuperscript{2+}, (bottom) the crude reaction mixture obtained by mixing 3, 7, 9 and Zn(BF\textsubscript{4})\textsubscript{2} in the molar ratio 2:1:1:1 at 60 °C for 18 h. The diagnostic signals of the heteroleptic complex [Zn(2,3)(2,7)]\textsuperscript{2+} are colored in orange.
Figure S47. Partial HRESI-MS spectra of the reaction mixture obtained by mixing 3, 7, 9 and Zn(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

Figure S48. $^1$H NMR (500 MHz, 297 K, CD$_3$CN) of the reaction mixture obtained by mixing 3, 7, 9 and Zn(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.

Figure S49. $^{13}$C NMR (125 MHz, 297 K, CD$_3$CN) of the reaction mixture obtained by mixing 3, 7, 9 and Zn(BF$_4$)$_2$ in the molar ratio 2:1:1:1 at 60 °C for 18 h.
3. Self-sorting reactions

3.1 General synthetic procedure

[Diagram showing chemical reaction]

Scheme S6. Synthesis of mononuclear complexes \([M(L)_2]^{n+}\) and \([M'(L)_2]^{n+}\) through the self-sorting of their initial reactants.

*General synthetic procedure:* CD$_3$CN solutions of each of the 2-formylpyridine containing components (100 µL of 32 mM, 3.2 µmol, 2 eq.) and of each of the amine containing components (100 µL of 32 mM, 3.2 µmol, 2 eq.) were combined. The resulting mixture was treated with CD$_3$CN solutions of each of the metal salts (100 µL of 16 mM, 1.6 µmol, 1 eq.) and heated at 60 °C for 18 h. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

3.2 Self-sorting of complexes \([Cu(1,4)_2]^+\) and \([Fe(2,3)_2]^{2+}\)

3.2.1 Simultaneous generation of complexes \([Cu(1,4)_2]^+\) and \([Fe(2,3)_2]^{2+}\) at 2.7 mM

[Diagram showing NMR spectra]

Figure S50. Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 297 K) of: (top) complex \([Fe(2,3)_2]^{2+}\), (middle) complex \([Cu(1,4)_2]^+\), (bottom) the crude reaction mixture of the attempted Simultaneous generation of complexes \([Cu(1,4)_2]^+\) and \([Fe(2,3)_2]^{2+}\) through the self-sorting of their initial reactants (2.7 mM). Reaction conditions: 1:2:3:4:Cu(BF$_4$):Fe(BF$_4$)$_2$ (2:2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, \([Cu(1,4)_2]^+\) in red, \([Fe(2,3)_2]^{2+}\) in purple and \([Fe(2,3)(2,4)]^{2+}\) in orange, one of the diagnostic signals of the free aldehydes 3 and 4 are highlighted by a grey circle.
3.2.2 Effect of concentration on the self-sorting of complexes \([\text{Cu}(1,4)_2]^+\) and \([\text{Fe}(2,3)_2]^{2+}\)

3.2.2.1 Simultaneous generation of complexes \([\text{Cu}(1,4)_2]^+\) and \([\text{Fe}(2,3)_2]^{2+}\) at 3.6 mM

CD$_3$CN solutions of the 2-formylpyridine containing components 3 (10 µL of 320 mM, 3.2 µmol, 2 eq.) and 4 (10 µL of 320 mM, 3.2 µmol, 2 eq.) and of the amine containing components 1 (10 µL of 320 mM, 3.2 µmol, 2 eq.) and 2 (10 µL of 320 mM, 3.2 µmol, 2 eq.) were combined. The resulting mixture was treated with CD$_3$CN solutions of CuBF$_4$ (20 µL of 80 mM, 1.6 µmol, 1 eq.) and Fe(BF$_4$)$_2$ (20 µL of 80 mM, 1.6 µmol, 1 eq.) before being diluted with 360 µL of CD$_3$CN and heated at 60 °C for up to 20 days. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

Figure S51. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (A) complex \([\text{Cu}(1,4)_2]^+\), (B) complex \([\text{Fe}(2,3)_2]^{2+}\), the crude reaction mixture obtained by reacting components 1, 2, 3 and 4 with Cu(BF$_4$) and Fe(BF$_4$)$_2$ in the molar ration 2:2:2:1:1 (3.6 mM) at 60 °C for 18 h (C), 4 days (D), 10 days (E) and 20 days (F). Diagnostic signals of the complexes are colour coded, \([\text{Cu}(1,4)_2]^+\) in red, \([\text{Fe}(2,3)_2]^{2+}\) in purple. Three
of the diagnostic signals of $[\text{Fe}^{2+}(2,3)(2,4)]^{2+}$ are colour coded in orange. One of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon and two of the diagnostic signals of the free amine 1 are highlighted by grey squares.

3.2.2.2 Probing the selectivity of the self-assembly of $[\text{Cu}(5,7)]^{+}$ and $[\text{Fe}(2,3)]^{2+}$ from a mixture of components 1, 2, 3 and 7 at 3.6 mM

**Figure S52.** Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (A) complex $[\text{Cu}(1,4)]^{+}$, the crude reaction mixture obtained by reacting components 1, 2, 3 and 4 with Cu(BF$_4$) in the molar ration 2:2:2:2:1 (3.6 mM) at 60 °C for 18 h (B), 4 days (C), 10 days (D) and 20 days (E). One of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle, one of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon, two of the diagnostic signals of the free amine 2 are highlighted by brown squares and two of the diagnostic signals of the free amine 1 are highlighted by grey squares.
Figure S53. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (A) complex [Fe(2,3)$_2$]$_2^{2+}$, the crude reaction mixture obtained by reacting components 1, 2, 3 and 4 with Fe(BF$_4$)$_2$ in the molar ratio 2:2:2:1 (3.6 mM) at 60 °C for 18 h (B), 4 days (C), 10 days (D) and 20 days (E). Diagnostic signals of the complex [Fe(2,3)$_2$]$_2^{2+}$ are colour coded in purple. Three of the diagnostic signals of [Fe(2,3)(2,4)]$_2^{2+}$ are colour coded in orange. One of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon and one of the diagnostic signals of the imine constituent (1,4) is highlighted by an orange star.
3.2.2.3 Simultaneous generation of complexes [Cu(1,4)]⁺ and [Fe(2,3)]²⁺ at 20 mM

Figure S54. Partial ¹H NMR spectra (500 MHz, CD₃CN, 297 K) of: (A) complex [Cu(1,4)]⁺, (B) complex [Fe(2,3)]²⁺, the crude reaction mixture obtained by reacting components 1, 2, 3 and 4 with Cu(BF₄) and Fe(BF₄)₂ in the molar ration 2:2:2:1:1 (20 mM) at 60 °C for 18 h (C), 4 days (D), 10 days (E) and 20 days (F). Diagnostic signals of the complexes are colour coded, [Cu(1,4)]⁺ in red, [Fe(2,3)]²⁺ in purple. Three of the diagnostic signals of [Fe(2,3)(2,4)]²⁺ are colour coded in orange. One of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon.
3.2.2.4 Probing the selectivity of the self-assembly of [Cu(5,7)]⁺ and [Fe(2,3)]²⁺ from a mixture of components 1, 2, 3 and 7 at 20 mM

CD₃CN solutions of the 2-formylpyridine containing components 3 (100 μL of 320 mM, 32 μmol, 2 eq.) and 4 (100 μL of 320 mM, 32 μmol, 2 eq.) and of the amine containing components 1 (100 μL of 320 mM, 32 μmol, 2 eq.) and 2 (10 μL of 320 mM, 32 μmol, 2 eq.) were combined. The resulting mixture was treated with CD₃CN solutions of CuBF₄ (200 μL of 80 mM, 16 μmol, 1 eq.) and Fe(BF₄)₂ (200 μL of 80 mM, 16 μmol, 1 eq.) and heated at 60 °C for up to 20 days. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

Figure S55. Partial ¹H NMR spectra (500 MHz, CD₃CN, 297 K) of: (A) complex [Cu(1,4)]⁺, the crude reaction mixture obtained by reacting components 1, 2, 3 and 4 with Cu(BF₄) in the molar ration 2:2:2:2:1 (20 mM) at 60 °C for 18 h (B), 4 days (C), 10 days (D) and 20 days (E). One of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle, one of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon, two of the diagnostic signals of the free amine 2 are highlighted by brown squares and two of the diagnostic signals of the free amine 1 are highlighted by grey squares.
**Figure S56.** Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (A) complex [Fe(2,3)$_2$]$^{2+}$, the crude reaction mixture obtained by reacting components 1, 2, 3 and 4 with Fe(BF$_4$)$_2$ in the molar ratio 2:2:2:2:1 (20 mM) at 60 °C for 18 h (B), 4 days (C), 10 days (D) and 20 days (E). Diagnostic signals of the complex [Fe(2,3)$_2$]$^{2+}$ are colour coded in purple. One of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon, one of the diagnostic signals of the imine constituent (1,4) is highlighted by an orange star.
3.3 Self-sorting of complexes $[\text{Cu}(4,5)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$

3.3.1 Simultaneous generation of complexes $[\text{Cu}(4,5)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$

![Diagram of complexes]

Figure S57. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (top) complex $[\text{Fe}(2,3)_2]^{2+}$, (middle) complex $[\text{Cu}(4,5)_2]^+$, (bottom) the crude reaction mixture of the simultaneous generation of complexes $[\text{Cu}(4,5)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$ through the self-sorting of their initial reactants. Reaction conditions:

$2:3:4:5:2\times\text{Cu(BF}_4\text{)}_2:2\times\text{Fe(BF}_4\text{)}_2$ (2:2:2:1:1), CD$_3$CN, 60 °C, 60 h. Diagnostic signals of the complexes are colour coded, $[\text{Cu}(4,5)_2]^+$ in red, $[\text{Fe}(2,3)_2]^{2+}$ in purple, one of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle and one of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon.
3.3.2 Monitoring of the formation of complexes \([\text{Cu}(4,5)_2]^+\) and \([\text{Fe}(2,3)_2]^{2+}\)

Figure S58. Formation of complexes \([\text{Cu}(4,5)_2]^+\) and \([\text{Fe}(2,3)_2]^{2+}\) from their initial reactants monitored by \(^1\text{H} \text{NMR}\) (600 MHz, CD\(_3\)CN, 333 K), aromatic region of the spectrum shown. The sample was maintained at 60 °C and spectra of the crude reaction mixture were recorded at increasing time increments (up to a final total time of 801 min). Reaction conditions: 2:3:4:5:Cu(BF\(_4\)):Fe(BF\(_4\))\(_2\) (2:2:2:1:1), CD\(_3\)CN, 60 °C. Diagnostic signals of the complexes are colour coded, \([\text{Cu}(4,5)_2]^+\) in red, \([\text{Fe}(2,3)_2]^{2+}\) in purple. Three of the diagnostic signals of the heteroleptic complex \([\text{Fe}(2,3)(2,5)]^{2+}\) are highlighted by orange stars. One of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle, one of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon.
Figure S59. Formation of complexes \([\text{Cu}(4,5)_2]^+\) and \([\text{Fe}(2,3)_2]^{2+}\) from their initial reactants monitored by \(^1\text{H NMR}\) (500 MHz, CD\(_3\)CN, 297 K), aromatic region of the spectrum shown. Spectra of the crude reaction mixture were collected after 21 h (top), 36 h (middle) and 60 h (bottom). Reaction conditions:

2:3:4:5:Cu\((\text{BF}_4)_2\):Fe\((\text{BF}_4)_2\) (2:2:2:2:1:1), CD\(_3\)CN, 60 °C. Three of the diagnostic signals of the complex \([\text{Fe}(2,3)(2,4)]^{2+}\) are highlighted by orange stars, one of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle and one of the diagnostic signals of the free aldehyde 4 is highlighted by a green pentagon.

Figure S60. Formation as a function of time of the thermodynamic products \([\text{Cu}(4,5)_2]^+\) (red squares) and \([\text{Fe}(2,3)_2]^{2+}\) (purple diamonds) and disappearance as a function of time of the kinetic product \([\text{Fe}(2,3)(2,4)]^{2+}\) (orange triangles). Graph plotting of the area of the imine peaks of the different complexes normalized to the area of the same peaks at the final time-point (after 60h).
3.4 Self-sorting of complexes $[\text{Cu}(1,6)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$

$[\text{Fe}(2,3)_2]^{2+}$

$[\text{Cu}(1,6)_2]^+$

Figure S61. Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 297 K) of: (top) complex $[\text{Fe}(2,3)_2]^{2+}$, (middle) complex $[\text{Cu}(1,6)_2]^+$, (bottom) the crude reaction mixture of the simultaneous generation of complexes $[\text{Cu}(1,6)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: $1:2:3:6:\text{Cu(BF}_4\text{)}_2:\text{Fe(BF}_4\text{)}_2$ (2:2:2:2:1), CD$_3$CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, $[\text{Cu}(1,6)_2]^+$ in red, $[\text{Fe}(2,3)_2]^{2+}$. One of the diagnostic signals of the free aldehyde 6 is highlighted by a grey circle and two of the diagnostic signals of the free aniline 1 are highlighted by grey squares.

3.5 Self-sorting of complexes $[\text{Cu}(1,7)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$

3.5.1 Simultaneous generation of complexes $[\text{Cu}(1,7)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$

$[\text{Fe}(2,3)_2]^{2+}$

$[\text{Cu}(1,7)_2]^+$

Figure S62. Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 297 K) of: (top) complex $[\text{Fe}(2,3)_2]^{2+}$, (middle) complex $[\text{Cu}(1,7)_2]^+$, (bottom) the crude reaction mixture of the simultaneous generation of complexes.
[Cu(1,7)₂]⁺ and [Fe(2,3)₂]²⁺ through the self-sorting of their initial reactants. Reaction conditions:
1:2:3:7:Cu(BF₄):Fe(BF₄)₂ (2:2:2:2:1:1), CD₃CN, 60 °C, 5 days. Diagnostic signals of the complexes are colour coded, [Cu(1,7)₂]⁺ in red, [Fe(2,3)₂]²⁺ in purple and three of the diagnostic signals of the heteroleptic complex [Fe(2,3)(2,7)]²⁺ are highlighted by orange stars and one of the diagnostic signals of the free aldehyde 7 is highlighted by a grey circle.

3.5.2 Monitoring of the formation of complexes [Cu(1,7)₂]⁺ and [Fe(2,3)₂]²⁺

Figure S63. Formation of complexes [Cu(1,7)₂]⁺ and [Fe(2,3)₂]²⁺ from their initial reactants monitored by
¹H NMR (400 MHz, CD₃CN, 297 K), aromatic region of the spectrum shown. Spectra of the crude reaction mixture were collected after 18 h (top), 5 days (middle) and 14 days (bottom). Reaction conditions:
1:2:3:7:Cu(BF₄):Fe(BF₄)₂ (2:2:2:2:1:1), CD₃CN, 60 °C.
3.6 Self-sorting of complexes [Cu(5,7)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$

3.6.1 Simultaneous generation of complexes [Cu(5,7)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$

Figure S64. Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 297 K) of: (top) complex [Fe(2,3)$_2$]$^{2+}$, (middle) complex [Cu(5,7)$_2$]$^+$, (bottom) the crude reaction mixture of the simultaneous generation of complexes [Cu(5,7)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: 2:3:5:7:Cu(BF$_4$):Fe(BF$_4$)$_2$ (2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, [Cu(5,7)$_2$]$^+$ in red, [Fe(2,3)$_2$]$^{2+}$ in purple.
3.6.2 Monitoring of the formation of complexes [Cu(5,7)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$

$t = 801$ min

$t = 605$ min

$t = 383$ min

$t = 240$ min

$t = 145$ min

$t = 80$ min

$t = 38$ min

$t = 0$s

Figure S65. Formation of complexes [Cu(5,7)$_2$]$^+$ and [Fe(2,3)$_2$]$^{2+}$ from their initial reactants monitored by $^1$H NMR ($400$ MHz, CD$_3$CN, 333 K), aromatic region of the spectrum shown. The sample was maintained at 60 °C and spectra of the crude reaction mixture were recorded at increasing time increments (up to a final total time of 801 min). Reaction conditions: 2:3:5:7:Cu(BF$_4$):Fe(BF$_4$)$_2$ (2:2:2:1:1), CD$_3$CN, 60 °C. Diagnostic signals of the complexes are colour coded, [Cu(5,7)$_2$]$^+$ in red, [Fe(2,3)$_2$]$^{2+}$ in purple. Diagnostic signals of the heteroleptic complex [Fe(2,3)(2,7)]$^{2+}$ are highlighted by orange stars. One of the diagnostic signals of the free aldehyde 7 is highlighted by a grey circle and one of the diagnostic signals of the free aldehyde 3 is highlighted by a green pentagon.
3.6.3 Probing of the selectivity of the self-assembly of [Cu(5,7)]⁺ and [Fe(2,3)]²⁺ from a mixture of components 1, 2, 3 and 7

Figure S66. Formation as a function of time of thermodynamic products [Cu(5,7)]⁺ (red squares) and [Fe(2,3)]²⁺ (purple diamonds) and disappearance as a function of time of the kinetic product [Fe(2,3)(2,7)]²⁺ (orange triangles). Graph plotting of the area of the imine peaks of the different complexes normalized to the area of the same peaks at the final time-point.

Figure S67. Partial ¹H NMR spectra (400 MHz, CD₃CN, 297 K) of: (A) complex [Fe(2,3)]²⁺, (B) the crude reaction mixture obtained by mixing 2:3:5:7:Fe(BF₄)₂ in the molar ratio 2:2:2:2:1 at 60 °C for 18 h, (C)
complex [Cu(5,7)]+ and (D) the crude reaction mixture obtained by mixing 2:3:5:7:Cu(BF₄) in the molar ratio 2:2:2:2:1 at 60 °C for 18 h. The diagnostic signals of the complex [Fe(2,3)]²⁺ are colour coded in purple.

3.7 Self-sorting of complexes [Cu(7,8)]⁺ and [Fe(2,3)]²⁺

3.7.1 Simultaneous generation of complexes [Cu(7,8)]⁺ and [Fe(2,3)]²⁺

![Diagram showing ¹H NMR spectra of complexes and crude reaction mixture.]

*Figure S68.* Partial ¹H NMR spectra (400 MHz, CD₃CN, 297 K) of: (top) complex [Fe(2,3)]²⁺, (middle) complex [Cu(7,8)]⁺, (bottom) the crude reaction mixture of the simultaneous generation of complexes [Cu(7,8)]⁺ and [Fe(2,3)]²⁺ through the self-sorting of their initial reactants. Reaction conditions: 2:3:7:8:Cu(BF₄):Fe(BF₄)₂ (2:2:2:1:1), CD₃CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, [Cu(7,8)]⁺ in red, [Fe(2,3)]²⁺ in purple. One of the diagnostic signals of the free aldehyde 7 is highlighted by a grey circle and two of the diagnostic signals of the free aniline 8 are highlighted by grey squares.
3.7.2 Monitoring of the formation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$

Figure S69. Formation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Fe}(2,3)_2]^{2+}$ from their initial reactants monitored by $^1$H NMR (500 MHz, CD$_3$CN, 333 K), aromatic region of the spectrum shown. The sample was maintained at 60 °C and spectra of the crude reaction mixture were recorded at increasing time increments (up to a final total time of 801 min). Reaction conditions: 2:3:7:8:Cu(BF$_4$)$_2$:Fe(BF$_4$)$_2$ (2:2:2:2:1:1), CD$_3$CN, 60 °C.

Diagnostic signals of the complexes are colour coded, $[\text{Cu}(7,8)_2]^+$ in red, $[\text{Fe}(2,3)_2]^{2+}$ in purple. Diagnostic signals of the heteroleptic complex $[\text{Fe}(2,3)(2,7)]^{2+}$ are highlighted by orange stars. One of the diagnostic signals of the free aldehyde 7 is highlighted by a grey circle, one of the diagnostic signals of the free aldehyde 3 is highlighted by a green pentagon and two of the diagnostic signals of the free aniline 8 are highlighted by grey squares.
**Figure S70.** Formation as a function of time of the thermodynamic products \([Cu(7,8)]^+\) (red squares) and \([Fe(2,3)]^{2+}\) (purple diamonds) and disappearance as a function of time of the kinetic product \([Fe(2,3)(2,7)]^{2+}\) (orange triangles). Graph plotting of the area of the imine peaks of the different complexes normalized to the area of the same peaks at the final time-point.

### 3.8 Self-sorting of complexes \([Cu(4,8)]^+\) and \([Fe(3,9)]^{2+}\)

![NMR spectra](image)

**Figure S71.** Partial \(^1\)H NMR spectra (400 MHz, CD\(_3\)CN, 297 K) of: (top) complex \([Fe(3,9)]^{2+}\), (middle) complex \([Cu(4,8)]^+\), (bottom) the crude reaction mixture of the simultaneous generation of complexes \([Cu(4,8)]^+\) and \([Fe(3,9)]^{2+}\) through the self-sorting of their initial reactants. Reaction conditions: 3:4:8:9:Cu(BF\(_4\)):Fe(BF\(_4\))\(_2\) (2:2:2:1:1), CD\(_3\)CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour-coded, \([Cu(4,8)]^+\) in red, \([Fe(3,9)]^{2+}\) in purple.
3.9 Self-sorting of complexes [Cu(7,8)$_2$]$^+$ and [Fe(3,9)$_2$]$^{2+}$

3.9.1 Simultaneous generation of complexes [Cu(7,8)$_2$]$^+$ and [Fe(3,9)$_2$]$^{2+}$

Figure S72. Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 297 K) of: (top) complex [Fe(3,9)$_2$]$^{2+}$, (middle) complex [Cu(7,8)$_2$]$^+$, (bottom) the crude reaction mixture of the simultaneous generation of complexes [Cu(7,8)$_2$]$^+$ and [Fe(3,9)$_2$]$^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: 3:7:8:9:Cu(BF$_4$):Fe(BF$_4$)$_2$ (2:2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, [Cu(7,8)$_2$]$^+$ in red, [Fe(3,9)$_2$]$^{2+}$ in purple.
3.9.2 Monitoring of the formation of complexes [Cu(7,8)₂⁺] and [Fe(3,9)₂²⁺]

Figure S73. Formation of complexes [Cu(7,8)₂⁺] and [Fe(3,9)₂²⁺] from their initial reactants monitored by ¹H NMR (400 MHz, CD₃CN, 333 K), aromatic region of the spectrum shown. The sample was maintained at 60 °C and spectra of the crude reaction mixture were recorded at increasing time increments (up to a final total time of 801 min). Reaction conditions: 3:7:8:9:Cu(BF₄):Fe(BF₄)₂ (2:2:2:1:1), CD₃CN, 60 °C.

Diagnostic signals of the complexes are colour coded, [Cu(7,8)₂⁺] in red, [Fe(3,9)₂²⁺] in purple. One of the diagnostic signals of the free aldehyde 7 is highlighted by a grey circle.
Figure S74. Formation as a function of time of the thermodynamic products \([\text{Cu}(7,8)_{2}]^{2+}\) (red diamonds) and \([\text{Fe}(3,9)_{2}]^{2+}\) (purple squares). Graph plotting of the area of the imine peak of \([\text{Fe}(3,9)_{2}]^{2+}\) and of the proton H\(^7\) of \([\text{Cu}(7,8)_{2}]^{2+}\) normalized to the area of the same peaks at the final time-point.

3.10 Comparison of the rate of formation of bis-2,2′:6′2″-terpyridine-like Fe\(^{II}\) complexes

Figure S75. Formation as a function of time of bis-2,2′:6′2″-terpyridine-like Fe\(^{II}\) complexes: \([\text{Fe}(3,10)_{2}]^{2+}\) from 3:7:8:10:Cu(BF\(_4\)):Fe(BF\(_4\))\(_2\) in the molar ratio 2:2:2:2:1:1 in CD\(_3\)CN at 60 °C (dark blue triangles), \([\text{Fe}(2,3)_{2}]^{2+}\) from 2:3:5:7:Cu(BF\(_4\)):Fe(BF\(_4\))\(_2\) in the molar ratio 2:2:2:2:1:1 in CD\(_3\)CN at 60 °C (dark grey lines), \([\text{Fe}(2,3)_{2}]^{2+}\) from 2:3:7:8:Cu(BF\(_4\)):Fe(BF\(_4\))\(_2\) in the molar ratio 2:2:2:2:1:1 in CD\(_3\)CN at 60 °C (light blue diamonds) and 2:3:4:5:Cu(BF\(_4\)):Fe(BF\(_4\))\(_2\) in the molar ratio 2:2:2:2:1:1 in CD\(_3\)CN at 60 °C (light grey squares). Graph plotting of the area of the imine peaks of the different complexes normalized to the area of the same peaks at the final time-point. See section 3.1.8, 3.1.6, 3.1.7 and 3.1.3, respectively, for more details on each individual reactions.
3.11 Self-sorting of complexes [Ag(7,8)\(_2\)]\(^+\) and [Fe(2,3)\(_2\)]\(^{2+}\)

![Diagram of complexes][1]

Figure S76. Partial \(^1\)H NMR spectra (400 MHz, CD\(_3\)CN, 297 K) of: (top) complex [Fe(2,3)\(_2\)]\(^{2+}\), (middle) complex [Ag(7,8)\(_2\)]\(^+\), (bottom) the crude reaction mixture of the simultaneous generation of complexes [Ag(7,8)\(_2\)]\(^+\) and [Fe(2,3)\(_2\)]\(^{2+}\) through the self-sorting of their initial reactants. Reaction conditions: 2:3:7:8:Ag(BF\(_4\)):Fe(BF\(_4\))\(_2\) (2:2:2:1:1), CD\(_3\)CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, [Ag(7,8)\(_2\)]\(^+\) in orange, [Fe(2,3)\(_2\)]\(^{2+}\) in purple. One of the diagnostic signals of the free aldehyde 7 is highlighted by a grey circle.

3.12 Self-sorting of complexes [Cu(7,8)\(_2\)]\(^+\) and [Zn(2,3)\(_2\)]\(^{2+}\)

3.12.1 Simultaneous generation of complexes [Cu(7,8)\(_2\)]\(^+\) and [Zn(2,3)\(_2\)]\(^{2+}\)

![Diagram of complexes][2]

Figure S77. Partial \(^1\)H NMR spectra (400 MHz, CD\(_3\)CN, 297 K) of: (top) complex [Zn(2,3)\(_2\)]\(^{2+}\), (middle)
complex $[\text{Cu}(7,8)_2]^+$, (bottom) the crude reaction mixture of the simultaneous generation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(2,3)_2]^{2+}$ through the self-sorting of their initial reactants. Reaction conditions: $2:3:7:8: \text{Cu(BF}_4\text{)}_2: \text{Zn(BF}_4\text{)}_2$ (2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, $[\text{Cu}(7,8)_2]^+$ in red, $[\text{Zn}(2,3)_2]^{2+}$ in green.

### 3.12.2 Monitoring of the formation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(2,3)_2]^{2+}$

| Time | Spectrum |
|------|----------|
| 18 h at 60 °C | ![Spectrum](image1.png) |
| 5 days at 60 °C | ![Spectrum](image2.png) |

**Figure S78.** Formation of complexes $[\text{Cu}(7,8)_2]^+$ and $[\text{Zn}(2,3)_2]^{2+}$ from their initial reactants monitored by $^1$H NMR (400 MHz, CD$_3$CN, 297 K), aromatic region of the spectrum shown. Spectra of the crude reaction mixture were collected after 18 h (upper) and 5 days (lower). Reaction conditions: $1:2:3:7: \text{Cu(BF}_4\text{)}_2: \text{Fe(BF}_4\text{)}_2$ (2:2:2:1:1), CD$_3$CN, 60 °C.

3.12.2.1 Probing the selectivity of Zn$^{II}$ cations for aldehyde 3 over aldehyde 7 in the presence of aminoquinoline 2

3.12.2.2 Procedure

**Scheme S7.** Probing the selectivity of Zn$^{II}$ cations for aldehyde 3 over aldehyde 7 in the presence of aminoquinoline 2. Distribution of the products generated by mixing 2, 3, 7 and Zn(BF$_4$)$_2$ in the molar ratio 2:2:2:1 at 60 °C for 6 days. Error on % determination: ±3%.

CD$_3$CN solutions of the 2-formylpyridine containing components 3 (50 µL of 32 mM, 1.6 µmol, 1 eq.) and 7 (50 µL of 32 mM, 3.2 µmol, 1 eq.) and of the aminoquinoline 2 (100 µL of 32 mM, 3.2 µmol, 2 eq.) were combined. The resulting mixture was treated with CD$_3$CN solutions of $[\text{Zn(C}_2\text{H}_6\text{OS})_2](\text{BF}_4)_2$ (100 µL of 32
mM, 3.2 µmol, 2 eq.) and heated at 60 °C for up to 6 days. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

Figure S79. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (upper) complex [Zn(2,3)$_2$]${}^{2+}$ and (lower) the crude reaction mixture obtained by mixing 2, 3, 7 and Zn(BF$_4$)$_2$ in the molar ratio 2:2:2:1 at 60 °C for 6 days. Diagnostic signals of the complex [Zn(2,3)$_2$]${}^{2+}$ are colour coded in green, two of the diagnostic signals of [Zn(2,3)(2,7)]${}^{2+}$ are highlighted by orange stars, one of the diagnostic signals of [Zn(2,7)$_2$]${}^{2+}$ is highlighted by a brown square, one of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle and one of the diagnostic signals of the free aldehyde 7 is highlighted by a green pentagon.

3.12.2.3 Monitoring of the formation of the complex [Zn(2,3)$_2$]${}^{2+}$

Figure S80. Formation of complex [Zn(2,3)$_2$]${}^{2+}$ from a mixture of 2, 3, 7 and Zn(BF$_4$)$_2$ in the molar ratio 2:2:2:1 monitored by $^1$H NMR (500 MHz, CD$_3$CN, 297 K), aromatic region of the spectrum shown. Spectra of the crude reaction mixture were collected after 2 days (top), 4 days (middle) and 6 days (bottom). Reaction conditions: 2:3:7:Zn(BF$_4$)$_2$ (2:2:2:1), CD$_3$CN, 60 °C.
3.13 Self-sorting of complexes \([\text{Cu}(7,8)_2]^{\text{+}}\) and \([\text{Zn}(3,9)_2]^{2\text{+}}\)

3.13.1 Simultaneous generation of complexes \([\text{Cu}(7,8)_2]^{\text{+}}\) and \([\text{Zn}(3,9)_2]^{2\text{+}}\)

\[
\text{[Zn(3,9)_2]}^{2\text{+}}
\]

\[
\text{[Cu(7,8)_2]}^{\text{+}}
\]

Figure S81. Partial 1H NMR spectra (400 MHz, CD$_3$CN, 297 K) of: (top) complex \([\text{Zn}(3,9)_2]^{2\text{+}}\), (middle) complex \([\text{Cu}(7,8)_2]^{\text{+}}\), (bottom) the crude reaction mixture of the simultaneous generation of complexes \([\text{Cu}(7,8)_2]^{\text{+}}\) and \([\text{Zn}(3,9)_2]^{2\text{+}}\) through the self-sorting of their initial reactants. Reaction conditions:

3:7:8:9:Cu(BF$_4$)$_2$:Zn(BF$_4$)$_2$ (2:2:2:1:1), CD$_3$CN, 60 °C, 18 h. Diagnostic signals of the complexes are colour coded, \([\text{Cu}(7,8)_2]^{\text{+}}\) in red, \([\text{Zn}(3,9)_2]^{2\text{+}}\) in green.

3.13.2 Probing the selectivity of Zn$^{II}$ cations for aldehyde 3 over aldehyde 7 in the presence of aminoquinoline 9

Scheme S8. Probing the selectivity of Zn$^{II}$ cations for aldehyde 3 over aldehyde 7 in the presence of aminoquinoline 9. Distribution of the products generated by mixing 2:3:9:Zn(BF$_4$)$_2$ in the molar ratio 2:2:2:1 at 60 °C for 2 days. Error on % determination: ±3%.

CD$_3$CN solutions of 2-formylpyridine containing components 3 (50 µL of 32 mM, 1.6 µmol, 1 eq.) and 7 (50 µL of 32 mM, 3.2 µmol, 1 eq.) and of aminoquinoline 9 (100 µL of 32 mM, 3.2 µmol, 2 eq.) were
combined. The resulting mixture was treated with CD$_3$CN solutions of [Zn(C$_2$H$_6$OS)$_6$](BF$_4$)$_2$ (100 µL of 32 mM, 3.2 µmol, 2 eq.) and heated at 60 °C for up to 2 days. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

Figure S82. Partial $^1$H NMR spectra (500 MHz, CD$_3$CN, 297 K) of: (upper) complex [Zn(3,9)$_2$]$_2^{2+}$ and (lower) the crude reaction mixture obtained by mixing 2, 3, 9 and Zn(BF$_4$)$_2$ in the molar ratio 2:2:2:1 at 60 °C for 2 days. Diagnostic signals of the complex [Zn(3,9)$_2$]$_2^{2+}$ are colour coded in green, two of the diagnostic signals of [Zn(3,9)(7,9)]$_2^{2+}$ are highlighted by orange stars, one of the diagnostic signals of the free aldehyde 3 is highlighted by a grey circle and one of the diagnostic signals of the free aldehyde 7 is highlighted by a green pentagon.

4. References
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