

# Triple self-sorting in constitutional dynamic networks: parallel generation of Cu(I), Fe(II) and Zn(II) imine-based metal complexes

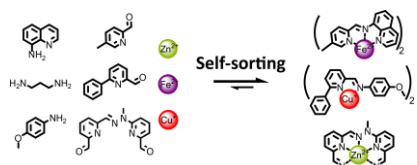
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Three imine-based metal complexes, having no overlap in term of their compositions, have been simultaneously generated from the self-sorting of a constitutional dynamic library containing three amines, three aldehydes and three metal salts. The mechanism and the driving forces underlying the self-sorting process have been examined.

## Abstract

Three imine-based metal complexes, having no overlap in terms of their compositions, have been simultaneously generated from the self-sorting of a constitutional dynamic library (CDL) containing three amines, three aldehydes and three metal salts. The hierarchical ordering of the stability of three metal complexes assembled and the leveraging of the antagonistic and agonistic relationships existing between the constituents within the constitutional dynamic network corresponding to the CDL were pivotal in achieving the desired sorting. The mechanism and the driving forces underlying the self-sorting process have been studied by NMR. The self-sorting of the Fe(II) and Zn(II) complexes was found to depend on an interplay between the thermodynamic driving forces and a kinetic trap involved in their assembling. These results also exemplify the concept of “simplicity” –the fact that the output of a self-assembling system may be simplified by increasing its initial compositional complexity—as the two complexes could self-sort only in the presence of the third pair of organic components, those of the Cu(I) complex.

## Introduction

The construction of dynamic networks of molecules presenting a high level of structural and functional complexity requires the development of strategies to control the organization and interconnection of sets of chemical entities having a high compositional and interactional diversity.<sup>[1]</sup> The application of the concepts of orthogonal self-assembly<sup>[2]</sup> and self-sorting<sup>[3-7]</sup> within the context of constitutional dynamic chemistry (CDC) provides a basis for such strategies.<sup>[1-8,9]</sup>

By operating through both reversible covalent bond formation and reversible supramolecular interactions, constitutional dynamic networks (CDNs) of molecules can be set up at both molecular and supramolecular levels. Prime examples of such multilevel organization can be found in CDNs created by the dynamic binding of metal cations to imine-based ligand constituents generated by the reversible condensation of amine and carbonyl (in particular 2-formylpyridine) containing components. Their high level of organization and their dynamic features have given access to architectures that would be otherwise inaccessible by traditional synthetic means and from which new properties have emerged.<sup>[7e-i,9b-e,10,11]</sup>

The concomitant assembling of multiple constitutional dynamic architectures has further extended the range of properties accessible with CDC,<sup>[1n,6d,9d,e,11a-d,q]</sup> highlighting the importance of fostering compositional diversity within such systems in order to access ever more complex features. However, increasing the compositional diversity of constitutional dynamic systems comes at an “informational cost”. As the system becomes more complex, more delicate structural and interactional information is required to prevent the crossover, within the different architectures, of components participating in dynamic processes that take place in the same domain. This cost grows rapidly as the number of architectures assembled through the same type of dynamic processes increases. For this reason, the majority of self-sorting systems involving constitutional dynamic metal-organic architectures known to date occur between architectures sharing one to two organic components and/or built around no more than two different types of metal cations.<sup>[3,6,7]</sup> This limited compositional diversity reflects the need for strategies to simultaneously control the outcome of two (or more) dynamic processes over multiple architectures, namely reversible covalent imine bond formation and dynamic metal-ligand coordination.

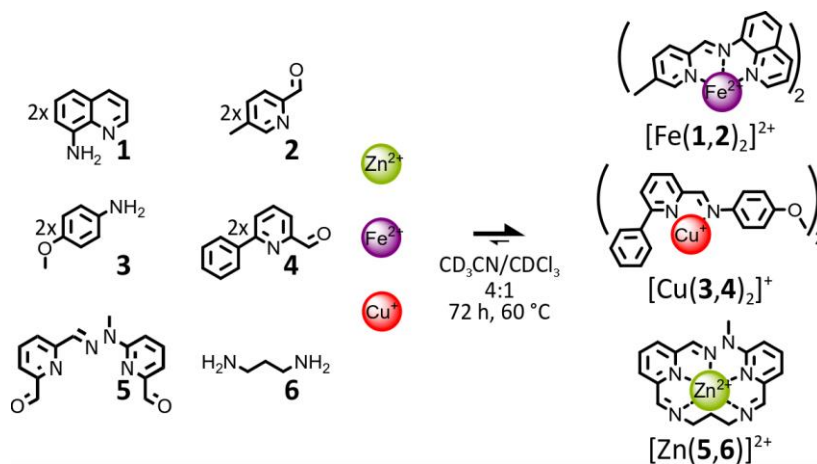
Here we demonstrate how the careful design of amine- and 2-formylpyridine-containing components, satisfying (or not), the unique coordination preferences of Cu(I), Fe(II) and Zn(II) ions, can enable the parallel generation of three imine-based metal complexes, that do not overlap in terms of their composition. The present study of the mechanism and the driving forces underlying the self-sorting process provides insights into the self-assembly pathways of each individual species within the mixture and reveals a subtle interplay between the thermodynamic driving forces and the kinetic traps involved.

## Results and Discussion

### *a. Rationale*

When a library of amine- and 2-formylpyridine-containing components is treated with different metal salts all the complexes formed share the same dynamic features (*i.e.* reversible imine bonds and dynamic metal—ligand interactions). Consequently, the complexes are able to exchange building blocks and thus they will develop either antagonistic or agonistic relationships depending on whether or not

they contain common building blocks. If they do share a component(s), the increase in the population of one of the complexes will occur at the expense of the population of the other one, these two complexes have an antagonistic relationship. If two complexes have no building block in common, they present an agonistic relationship: the formation of one complex in an agonistic pair will promote the formation of the other one by liberating, as it builds up, the unshared components that will form the agonistic complex. By exploiting these regulatory relationships between complexes, one can promote the formation of a complex that would normally not be expressed, by trapping all the other unshared components and metal cations in more stable complexes. These regulatory processes indicate that to achieve the parallel self-assembly of three fully non-identical imine-based metal complexes it may be sufficient that only one of these complexes be capable of self-assembling in the presence of the reactants of the two other ones. The work described in the present report demonstrates that it is the case. Indeed, if one complex is capable of selectively self-assembling from all the initial reactants, its formation will trap one type of metal cation and one pair of amine- and 2-formylpyridine-containing components in its structure. The next complex has then to be able to form selectively only from the remaining two types of metal, amine and aldehyde components. The self-assembly of the third complex does not even need to be selective as its composition will be imposed by the reactants left in solution by the two other metal cations. We envisage that the three metal complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  should present the appropriate hierarchical ordering of their stabilities to allow for such self-sorting (Scheme 1), the notation  $(\mathbf{n},\mathbf{m})$  refers to the imine-based constituent generated by the condensation of amine  $\mathbf{n}$  with aldehyde  $\mathbf{m}$  (in no specific order).



**Scheme 1.** Concomitant formation of complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  through the hetero-self-sorting of their initial reactants.

We have previously shown that by exploiting the difference in coordination number between tetrahedral and octahedral coordination geometries and by manipulating the steric hindrance features of two derivatives of 2-formylpyridine,  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  could be selectively self-assembled from their initial reactants.<sup>[12]</sup> The driving force of this self-sorting process was found to be the strong affinity of the Fe(II) metal cations for the sterically unhindered tridentate coordination site formed by the condensation of the aminoquinoline **1** with the 2-formylpyridine **2**. We also showed that the formation of the Cu(I) complex  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  was compatible with the simultaneous formation of imine-containing Zn(II) complexes.<sup>[12]</sup> Given that Zn(II) cations form a highly stable and selective macrocyclic

complex  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  with the dialdehyde **5** and the diamine **6**,<sup>[9e,11s-u]</sup> we presumed that the presence of Cu(I) cations and components **3** and **4** would not interfere with its formation. We also envisaged that the formation of the Fe(II) complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  would be possible in the presence of Zn(II) cations, dialdehyde **5** and diamine **6**, as low-spin  $d^6$  Fe(II) cations are expected to favor the formation of an octahedral complex with two terpyridine-like ligand (**1,2**) rather than a complex with the planar pentadentate macrocyclic ligand (**5,6**). Furthermore, the inclusion of the terpyridine-like components **5** in a Fe(II) complex would be disfavored due to the steric hindrance around its coordination site imposed by the substitution next to the nitrogen site in the pyridine groups. Finally, given that bis-terpyridine complexes of Fe(II) are more stable than their Zn(II) equivalents, the formation of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  should prevail over that of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ .<sup>[13]</sup>

On these bases, it appeared likely that the three complexes would be able to self-sort from a mixture of their initial components upon addition of the three appropriate metal salts.

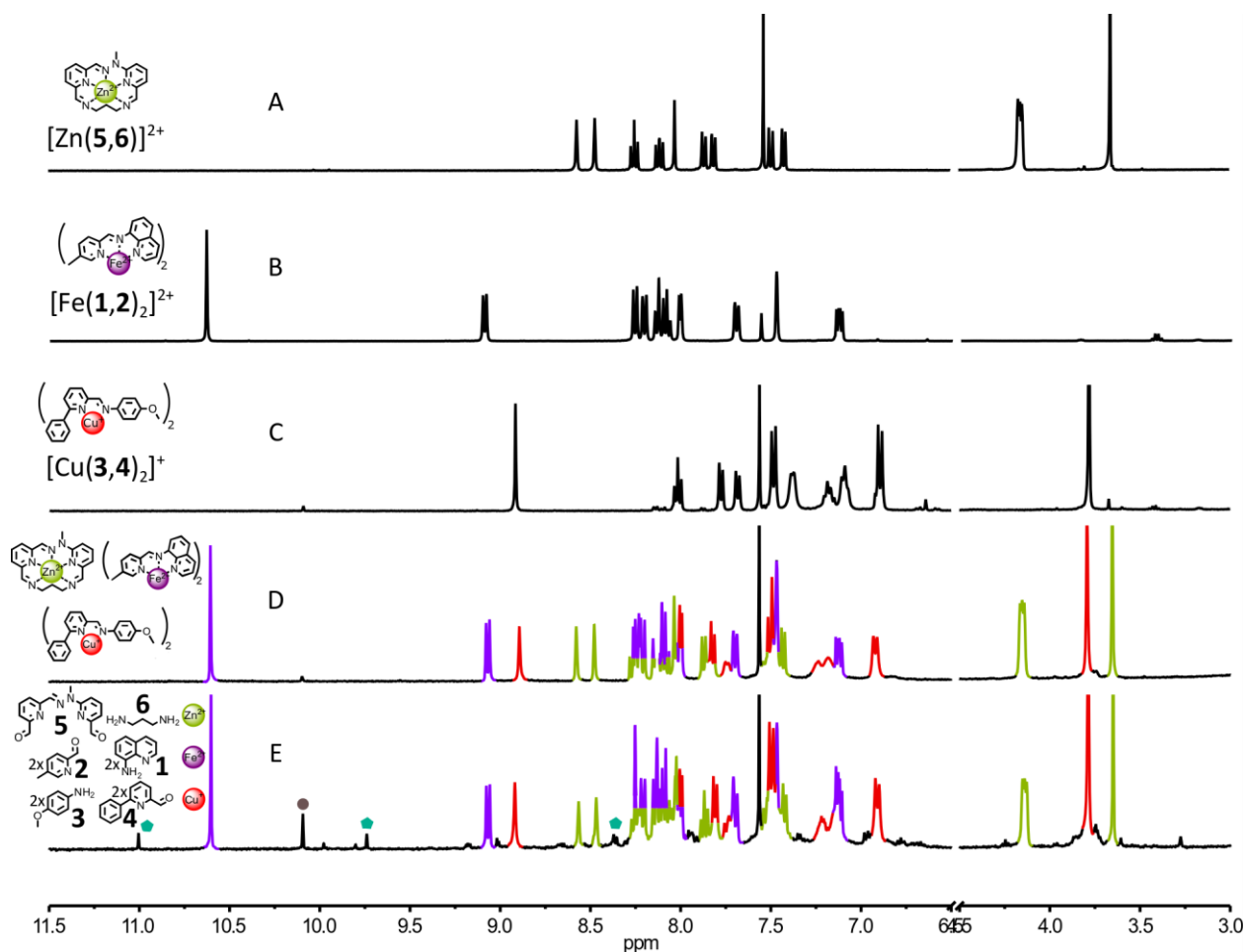
***b. Parallel self-assembly of three imine-containing complexes via hetero-self-sorting from an initial set of nine components, six molecular ones and three different metal cations***

The self-sorting potential of a CDL composed of the six molecular components **1-6** in a 2:2:2:2:1:1 ratio and 1 eq. each of  $\text{Fe}(\text{BF}_4)_2$ ,  $\text{Cu}(\text{BF}_4)$  and  $\text{Zn}(\text{BF}_4)_2$  was investigated by reacting the library in  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1) at 60 °C for 72 h. The  $^1\text{H}$  NMR spectrum of the crude reaction mixture indicated the generation of the three anticipated metal complexes as the diagnostic signals of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  dominated the spectrum of the reaction mixture (Figure 1E).

The initial pool of reactants was expected to yield the three complexes in a 1:1:1 ratio, however  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  were obtained in a 0,95:0,8:1 ratio. The smaller amount for  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  in solution could be attributed to the partial hydrolysis of the ligand (**3,4**) and to the presence of residual heteroleptic Fe(II) complex  $[\text{Fe}(\mathbf{1},\mathbf{2})(\mathbf{1},\mathbf{4})]^{2+}$  (this heteroleptic complex has been shown to appear as a kinetic product during the formation of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  from their reactants).<sup>[12]</sup> The sum of the amounts of aldehyde **4** observable as free component **4** and as part of  $[\text{Fe}(\mathbf{1},\mathbf{2})(\mathbf{1},\mathbf{4})]^{2+}$  matched with the amount of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  missing from the reaction mixture. The amount of the heteroleptic complex  $[\text{Fe}(\mathbf{1},\mathbf{2})(\mathbf{1},\mathbf{4})]^{2+}$  measured equalled the amount of the homoleptic complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  missing from the reaction mixture. Further heating of the reaction mixture at 60 °C for up to 6 days, helped to dissipate the residual heteroleptic complex  $[\text{Fe}(\mathbf{1},\mathbf{2})(\mathbf{1},\mathbf{4})]^{2+}$  but resulted in an increased decomposition of the complex  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  (see the Supporting Information).

A mixture of the preformed complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  in a 1:1:1 ratio (Figure 1D) was heated at 60°C and followed by  $^1\text{H}$  NMR for up to 72 h (see the Supporting Information). The distribution of three complexes mirrored the one obtained from the self-sorting-experiment and remained unchanged throughout the experiment, indicating that this state is the thermodynamic end point of the self-sorting process under the conditions used.

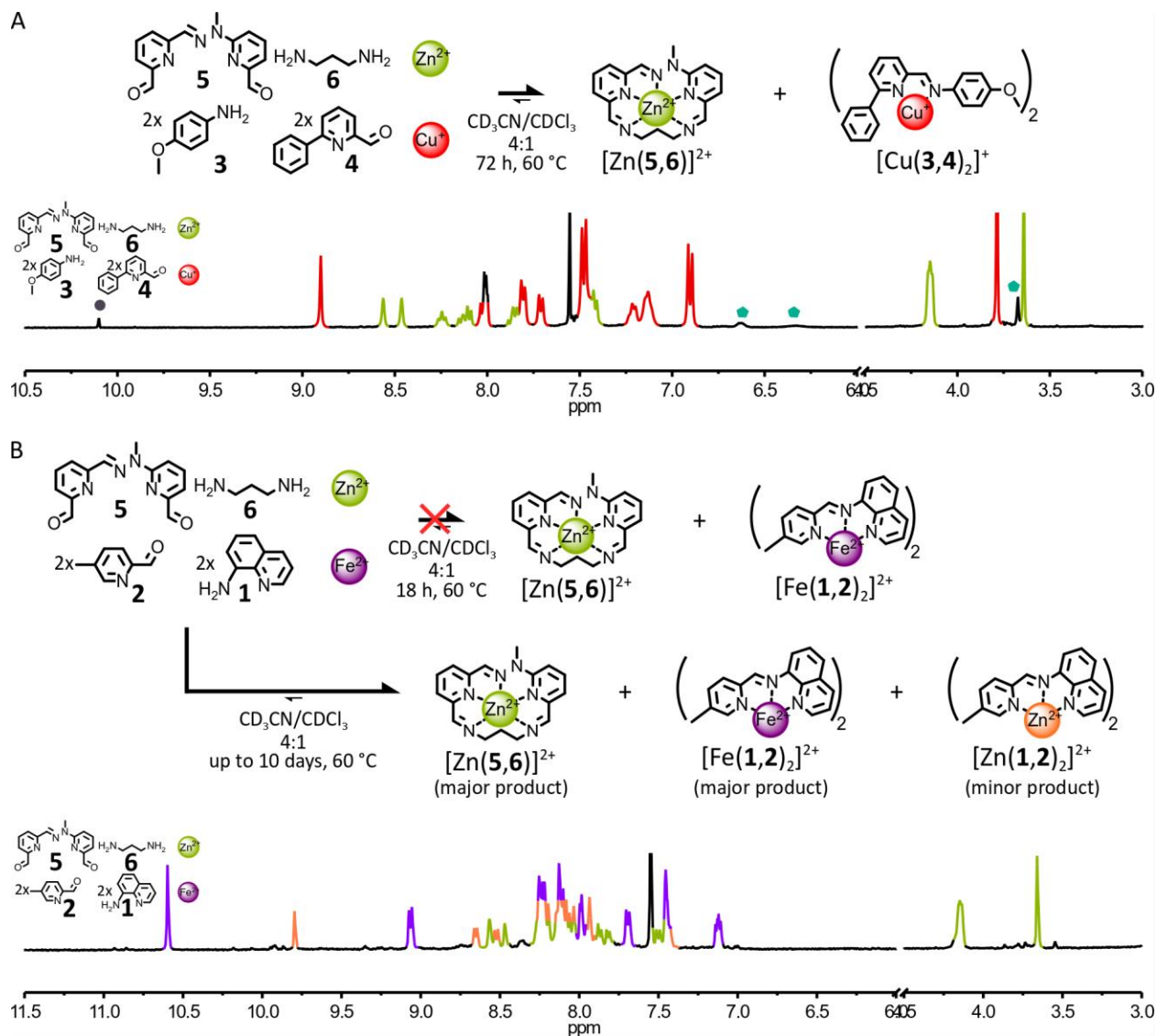
Starting from the components themselves and in the same conditions,  $\text{Ag}(\text{BF}_4)$  could be used as a substitute for  $\text{Cu}(\text{BF}_4)$ , leading to the formation of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Ag}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  as major products of the self-sorting process (see the Supporting Information). However, in this case significantly more free aldehyde **4** was observed in the  $^1\text{H}$  NMR of the reaction mixture compared to the system using Cu(I) cations and some unidentified side products were observed alongside the three complexes.



**Figure 1.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_3\text{CN}:\text{CDCl}_3$  4:1, 298 K) of: (A) complex  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$ , (B) complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ , (C) complex  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$ , (D) an equimolar solution of preformed complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ ,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  after 18 h at 60 °C, (E) the reaction mixture obtained from mixing components  $\mathbf{1}:\mathbf{2}:\mathbf{3}:\mathbf{4}:\mathbf{5}:\mathbf{6}:\text{Fe}(\text{BF}_4)_2:\text{Zn}(\text{BF}_4)_2:\text{Cu}(\text{BF}_4)_2$  in the molar ratio 2:2:2:2:1:1:1:1:1:1 ratio at 60 °C for 72 h. The diagnostic signals of the complexes are colour coded,  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  in purple,  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  in red and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  in green, one of the diagnostic signals of the free aldehyde  $\mathbf{4}$  is highlighted by a grey circle and some of the diagnostic signals of the heteroleptic complex  $[\text{Fe}(\mathbf{1},\mathbf{2})(\mathbf{1},\mathbf{4})]^{2+}$  are highlighted by a green pentagon.

### c. Probing of the relative selectivity of the self-assembly of the three complexes

To assess the relative stability of each complex with respect to the two other ones, their formation was studied in smaller systems of two complexes. The use of these sub-systems also allowed probing for the potential influence of the reagents of the third complex on the fidelity of the self-sorting of the two other ones.



**Figure 2.** (A) Parallel formation of complexes  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  through the self-sorting of their initial reactants. Reaction conditions:  $\mathbf{3}:\mathbf{4}:\mathbf{5}:\mathbf{6}:\text{Cu}(\text{BF}_4):\text{Zn}(\text{BF}_4)_2$  (2:2:1:1:1:1),  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1), 60 °C, 72 h. Lower - Partial  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1), 298 K) of the crude reaction mixture after 72 h at 60 °C, the diagnostic signals of the complexes are colour coded,  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  in green and  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  in red, one of the diagnostic signals of the free aldehyde  $\mathbf{4}$  is highlighted by a grey circle and diagnostic signals of the free aniline  $\mathbf{3}$  are highlighted by turquoise pentagons. (B) Upper - Simultaneous generation of complexes  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  through the self-sorting of their initial reactants. Reaction conditions:  $\mathbf{1}:\mathbf{2}:\mathbf{5}:\mathbf{6}:\text{Fe}(\text{BF}_4)_2:\text{Zn}(\text{BF}_4)_2$  (2:2:1:1:1:1),  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1), 60 °C, 10 days. Lower - Partial  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1), 298 K) of the crude reaction mixture after 10 days at 60 °C, the diagnostic signals of the complexes are colour coded,  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  in green,  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  in purple and  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  in orange.

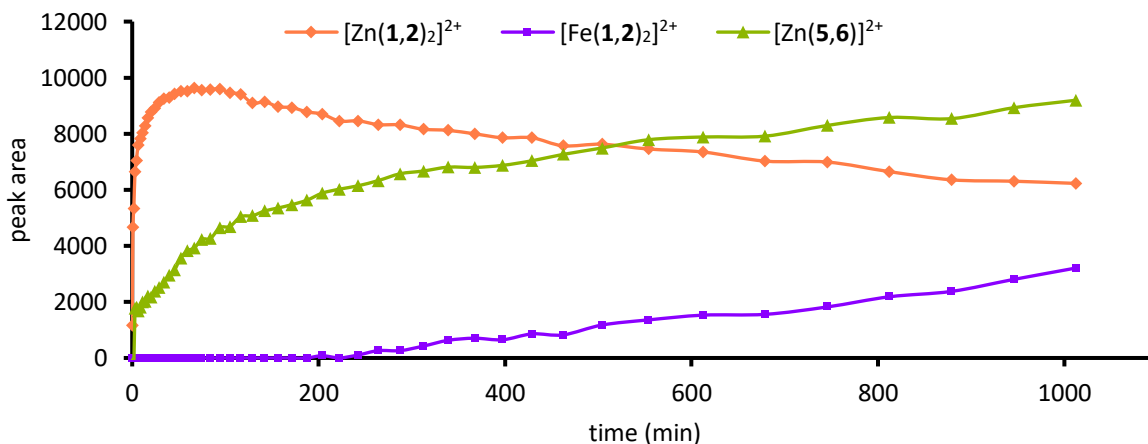
The Fe(II) complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and the Cu(I) complex  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  were known to self-sort from an equimolar mixture of their four initial components upon addition of 1 eq. Fe(II) and 1 eq. Cu(I) salts after 24 h at 60 °C.<sup>[12]</sup>

The selectivity of the self-assembly of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  from their reactants was probed by mixing components **3**, **4**, **5** and **6** in a 2:2:1:1 ratio in the presence of 1 eq. each of  $\text{Cu}(\text{BF}_4)$  and  $\text{Zn}(\text{BF}_4)_2$  (Figure 2A). After 72 h at 60 °C, most of the starting materials had been converted into a clean mixture of the two anticipated complexes  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$ . Beside the diagnostic signals of the two complexes, the  $^1\text{H}$  NMR spectrum of the crude reaction mixture revealed traces of free components **3** and **4** resulting from the hydrolysis of the imine of constituent (**3,4**). The high fidelity of the self-sorting process of this system can be attributed to the strong differences of coordination number and coordination geometries between the two metal cations.

To investigate the self-sorting potential of components **1**, **2**, **5** and **6** in the presence of Fe(II) cations and Zn(II) cations, a 2:2:1:1 mixture of these components was allowed to react with 1 eq. of  $\text{Fe}(\text{BF}_4)_2$  and 1 eq. of  $\text{Zn}(\text{BF}_4)_2$  in  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1) at 60 °C (Figure 2B). After 24 h, three species were observable in the  $^1\text{H}$  NMR spectrum of the crude reaction mixture. A significant amount of complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  could be seen beside the two anticipated complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  (see the Supporting Information). When the reaction mixture was subjected to further heating at 60 °C, the amount of complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  observable in solution by  $^1\text{H}$  NMR slowly declined overtime while the amount of complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  slowly rose, indicating that  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  formed as a kinetic product in the course of the self-assembly process. After 5 days of heating at 60 °C (see the Supporting Information), the composition of the reaction mixture was as follows: 75% of the initial components **1** and **2** were included in  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and the remaining 25% were incorporated in  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ .<sup>[14]</sup> 60% of the initial components **5** and **6** were associated with Zn(II) cations in  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$ . The remaining 40% of components **5** and **6** were not observable by  $^1\text{H}$  NMR as they precipitated out of solution under the form of the poorly soluble macrocyclic compound (**5<sub>2</sub>,6<sub>2</sub>**) (the macrocycle (**5<sub>2</sub>,6<sub>2</sub>**) has been shown to precipitate from mixtures of components **5** and **6** in 4:6  $\text{CD}_3\text{CN}:\text{CDCl}_3$ ).<sup>[11]</sup>

To confirm that the complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  is a kinetic product, the self-assembly of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  from their initial reagents was scrutinized over time by  $^1\text{H}$  NMR. Immediately upon mixing of the reactants, only  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  was detectable in the reaction mixture (Figure 3 and Supporting Information). After 90 mins of heating at 60 °C, its amount in solution reached its peak and a small amount of metallo-macrocyclic  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  was observable. At this point,  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  was still absent from the reaction mixture. After around 200 mins,  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  became detectable. From this point onward, the amount of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  in solution kept on diminishing while the amount of  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  in solution continued to increase. The overall kinetics of the reorganization process are very slow as a substantial amount of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  was still observable in the  $^1\text{H}$  NMR spectra of the reaction mixture after 10 days at 60 °C (Figure 2B).

To verify that  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  are the thermodynamic products of the reaction under the conditions used, the two complexes were prepared separately before being mixed in about a 1:1 ratio (see the Supporting Information). After 5 days of heating at 60 °C, the  $^1\text{H}$  NMR spectrum of the reaction mixture was a pristine superimposition of the spectra of the two individual complexes, indicating that  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  are indeed the thermodynamic products of the self-assembly process and that  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  is a kinetic product.

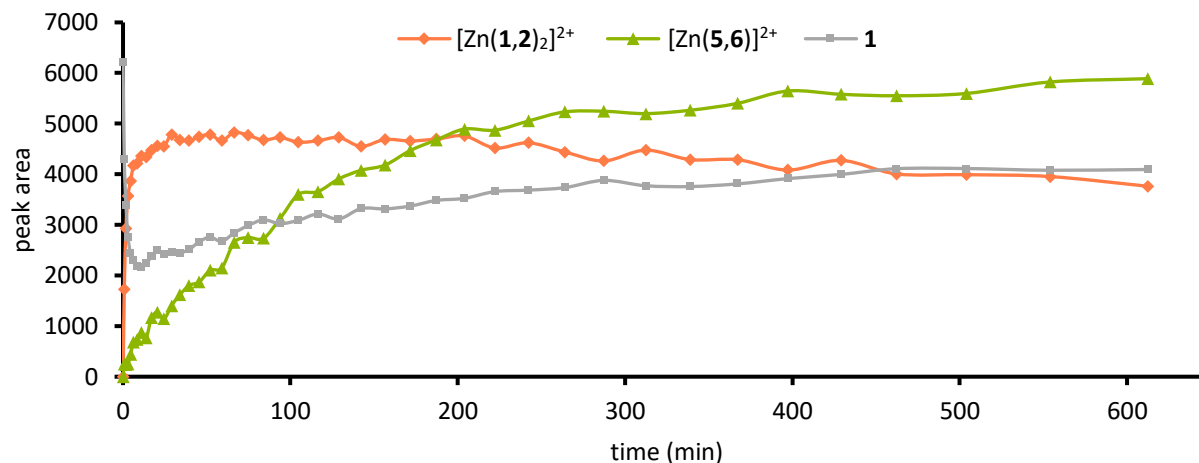


**Figure 3.** Formation as a function of time of the thermodynamic products  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  (purple squares) and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  (green triangles) and of kinetic product  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  (orange diamonds). Reaction conditions:  $\mathbf{1}:\mathbf{2}:\mathbf{5}:\mathbf{6}:\text{Fe}(\text{BF}_4)_2:\text{Zn}(\text{BF}_4)_2$  (2:2:1:1:1:1),  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1),  $60^\circ\text{C}$ . The  $^1\text{H}$  NMR spectrum of the reaction mixture was recorded at increasing time increments. Peak areas of the imine peaks for  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  and of the  $\text{NCH}_3$  peak for  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  as obtained from the  $^1\text{H}$  NMR spectra recorded.

To gather more information on the driving forces governing the self-assembly of  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and to evaluate the likelihood of reaching the thermodynamic end point of this self-sorting process, the formation of each of the two complexes was attempted by mixing 1 eq. of the corresponding metal salt with a 2:2:1:1 mixture of respectively  $\mathbf{1}$ ,  $\mathbf{2}$ ,  $\mathbf{5}$ ,  $\mathbf{6}$  in  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1) at  $60^\circ\text{C}$ . The evolution of the composition of the two reaction mixtures was monitored by  $^1\text{H}$  NMR spectroscopy over the course of 10 days.

First, the Zn(II) system was investigated. Immediately after the addition of the Zn(II) cations to the mixture of components the characteristic signals of complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  appeared in the  $^1\text{H}$  NMR spectrum of the reaction mixture (Figure 4 and Supporting Information). The amount of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  in solution peaked after about 30 min, before slowly declining until the end of the experiment (at about 10 h). The formation of the macrocyclic complex  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  was slower. The diagnostic signals of the metallo-macrocyclic complex appeared several minutes after the mixing of the reactants. However, contrary to  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ , the amount of  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  in solution kept on increasing steadily until the end of the experiment. The evolution of the amounts of individual components  $\mathbf{1}$  and  $\mathbf{2}$  in solution reflected closely that of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ . Components  $\mathbf{1}$  and  $\mathbf{2}$  were swiftly consumed at the beginning of the experiment, reaching their lowest concentration at about 15 min. Past this point, their concentration rose until the experiment was ended (at about 10 h). After 5 days of heating at  $60^\circ\text{C}$ , the signals of both complexes  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  were still observable in the  $^1\text{H}$  NMR spectra of the reaction, amounting respectively for the consumption of 55% and 45% of the initial Zn(II) cations.<sup>[14]</sup> The two complexes were observed alongside 45% of the initial components  $\mathbf{1}$  and  $\mathbf{2}$  and 25% of the initial component  $\mathbf{5}$ . The amount of the two complexes in solution did not change when the mixture was left to react for longer at  $60^\circ\text{C}$  (up to 10 days). As  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  were obtained in almost a 1:1 ratio, the stability of both complexes must be similar, thus Zn(II) cations alone cannot drive the Fe(II)/Zn(II) system towards its thermodynamic end point.

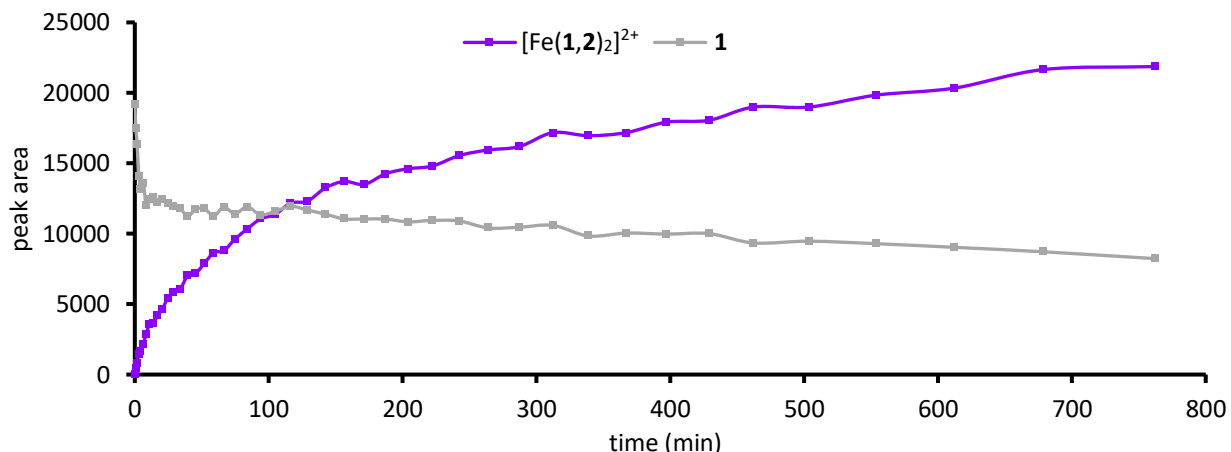




**Figure 4.** Formation as a function of time of the thermodynamic products  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  (green triangles) and of kinetic product  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  (orange diamonds) and rate of consumption of component **1** (grey squares). Reaction conditions: **1**:**2**:**5**:**6**: $\text{Zn}(\text{BF}_4)_2$  (2:2:1:1:1),  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1), 60 °C. The  $^1\text{H}$  NMR spectra of the reaction mixture was recorded at increasing time increments. Peak areas of the imine peaks for  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ , the  $\text{NCH}_3$  peak for  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and the CH peak for **1** as obtained from the  $^1\text{H}$  NMR spectra recorded.

Second, the Fe(II) system was studied. Minutes after the addition of Fe(II) cations to the initial mixture of components the characteristic signals of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  appeared in the  $^1\text{H}$  NMR spectrum of the reaction mixture (Figure 5 and Supporting Information). The concentration of the complex increased steadily throughout the experiment. The evolution of the concentration of free component **1** reflected that of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ . It swiftly decreased at the beginning of the experiment and then kept on diminishing but at a slower pace until the end (at about 10 h). The self-assembly of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  was selective. After 5 days of heating at 60 °C, 85% of the anticipated  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  had formed and was observed alongside 15% of the initial components **1** and **2** and 35% of the initial component **5**.<sup>[14]</sup> Prolonged heating at 60 °C (up to 10 days) did not yield any additional  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  complex. Under these conditions  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  appeared to be the thermodynamically most stable Fe(II) complex obtained from the initial library of components. Thus, Fe(II) cations should be able to drive the Fe(II)/Zn(II) system towards its thermodynamic end point given that  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  is more stable than  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ .

The stability of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  compared to  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  was probed by treating a solution of preformed complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  in  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1) with 1 eq. of  $\text{Zn}(\text{BF}_4)_2$  (see the Supporting Information). After 4 days at 60 °C, the  $^1\text{H}$  NMR spectrum of the mixture only contained the diagnostic signals of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ , indicating that it is more stable than  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ . The strong preference of the Fe(II) cations for the N-N-N tridentate constituent (**1,2**) should theoretically lead the Fe(II)/Zn(II) system towards the exclusive formation of  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ . However the slow kinetics of the recombination process of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  into  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  prevented the system from reaching its thermodynamic end point within a practical timeframe. In the Fe(II)/Cu(I)/Zn(II) system, some of the components of  $[\text{Cu}(\mathbf{5},\mathbf{6})]^{2+}$  must speed up the rearrangement of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  into  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  as this problem was not encountered in the initial system of three complexes.



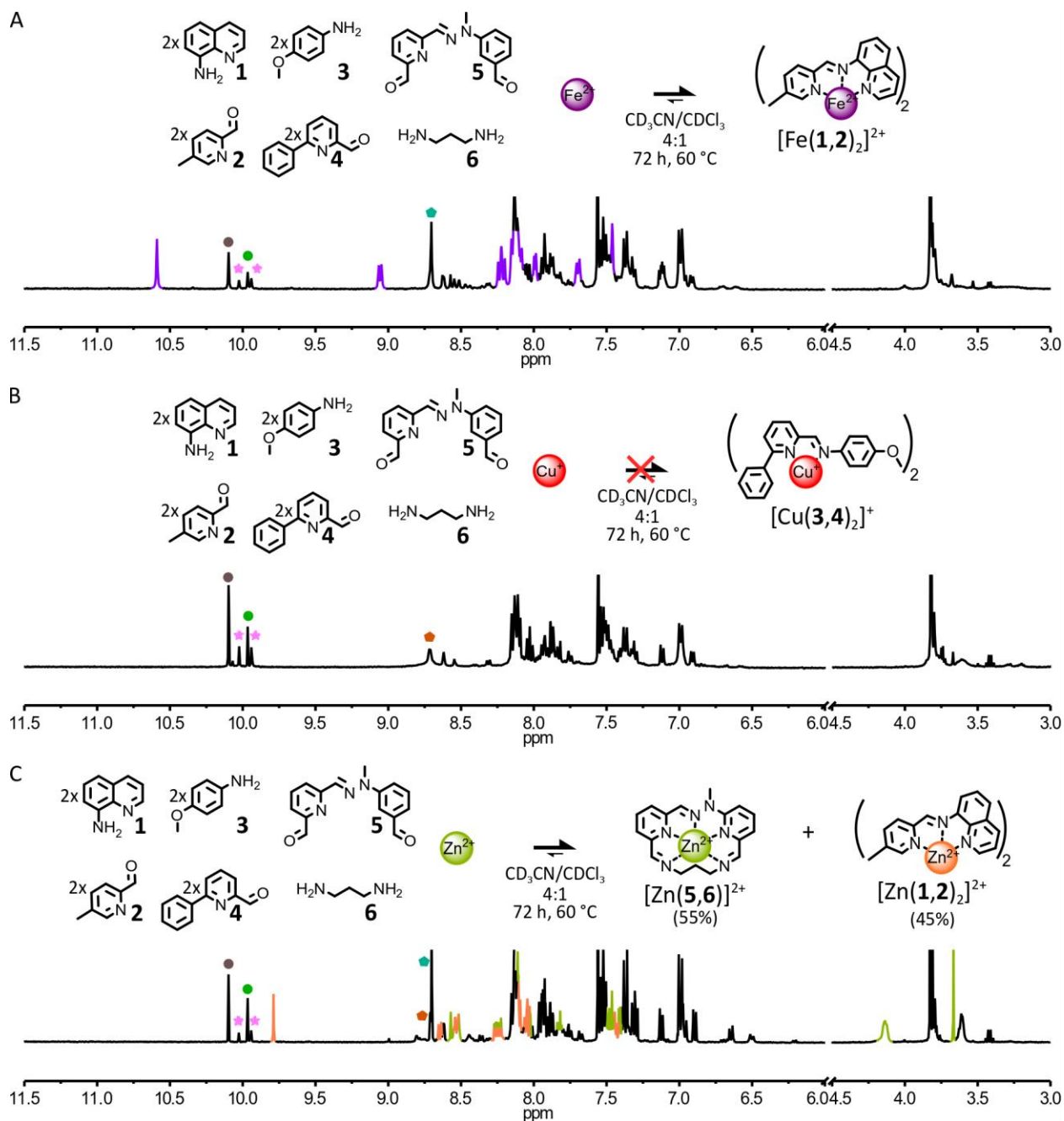
**Figure 5.** Formation as a function of time of the thermodynamic products  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  (purple squares) and rate of consumption of component **1** (grey squares). Reaction conditions: **1**:**2**:**5**:**6**: $\text{Fe}(\text{BF}_4)_2$  (2:2:1:1:1),  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1), 60 °C. The  $^1\text{H}$  NMR spectra of the reaction mixture was recorded at increasing time increments. Peak areas of the imine peaks for  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and the CH peak for **1** as obtained from the  $^1\text{H}$  NMR spectra recorded.

#### **d. Probing of the robustness of the self-assembly of the three complexes**

To assess the affinity of each metal cation for its preferred pair of components, a solution of components **1-6** in a 2:2:2:2:1:1 ratio in  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1) was treated with only one of the three metal cations. The resulting mixtures were left to react at 60 °C for up to 3 days and the evolution of their compositions was followed by  $^1\text{H}$  NMR spectroscopy.

When 1 eq. of  $\text{Fe}(\text{BF}_4)_2$  was added to the solution of the six organic components, the strong affinity of the Fe(II) ions for the imine constituent (**1,2**) ensured the formation of the major part of the anticipated  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  complex (Figure 6A).<sup>[14]</sup> After 3 days at 60 °C, about 85% of this complex had formed, alongside some unreacted aldehyde **2** (about 15% of the initial amount), about 50% unreacted aldehyde **4** and some imine constituent (**3,4**) (which could not be precisely quantified due to overlap with other signals of unknown byproducts). Only a small amount of **5** was observed in the  $^1\text{H}$  NMR spectrum of the reaction mixture as most of it precipitated out of solution due to the formation of the poorly soluble macrocycle (**5<sub>2</sub>,6<sub>2</sub>**). This experiment confirmed that  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  is the thermodynamically most stable Fe(II) complex obtainable from this library of components.

When the initial library of components was treated with 1 eq. of  $\text{Cu}(\text{BF}_4)$ , no traces of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$ , could be detected by  $^1\text{H}$  NMR spectroscopy (Figure 6B). The affinity of Cu(I) cations for the imine constituent (**3,4**) is too weak to allow the selective self-assembly of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  from the initial components. This result confirms that the formation of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  in the initial system (see results and discussion section b.) is the product of the antagonistic and agonistic regulatory relationships existing between the constituents of a CDN. Components **1**, **2**, **5** and **6** must be trapped into the form of the more stable Fe(II) and Zn(II) complexes to allow for the formation of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$ . This example demonstrates how CDNs can be leveraged to enforce the formation of thermodynamically unfavorable products.<sup>[9e,f]</sup>



**Figure 6.** (A) Upper - Formation of the complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  through the self-sorting of its components from a mixture of components **1-6**. Reaction conditions: **1:2:3:4:5:6:Fe**(BF<sub>4</sub>)<sub>2</sub> (2:2:2:2:1:1:1), CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 60 °C, 72 h. (B) Upper - Attempted generation of the complex  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  through the self-sorting of its components from a mixture of components **1-6**. Reaction conditions: **1-6** and Cu(BF<sub>4</sub>) (2:2:2:2:1:1:1), CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 60 °C, 72 h. (C) Upper - Attempted generation of the complex  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  through the self-sorting of its components from a mixture of components **1-6**. Reaction conditions: **1-6** and Zn(BF<sub>4</sub>)<sub>2</sub> (2:2:2:2:1:1:1), CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 60 °C, 72 h. (A), (B) and (C) Lower - Partial <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 298 K) of the crude reaction mixture after 72 h at 60 °C. The diagnostic signals of the complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  are coloured in purple. The diagnostic signals of the complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  and

$[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  are colour coded in orange and green respectively. Some of the diagnostic signals of the free aldehyde **2**, free aldehydes **4** and free bis-aldehyde **5** are respectively highlighted by a green circle, a grey circle, and pink stars, one of the diagnostic signals of free aminoquinoline **1** is highlighted by an orange pentagon and one of the diagnostic signals of the imine-containing constituent (**3,4**) is highlighted by a turquoise pentagon.

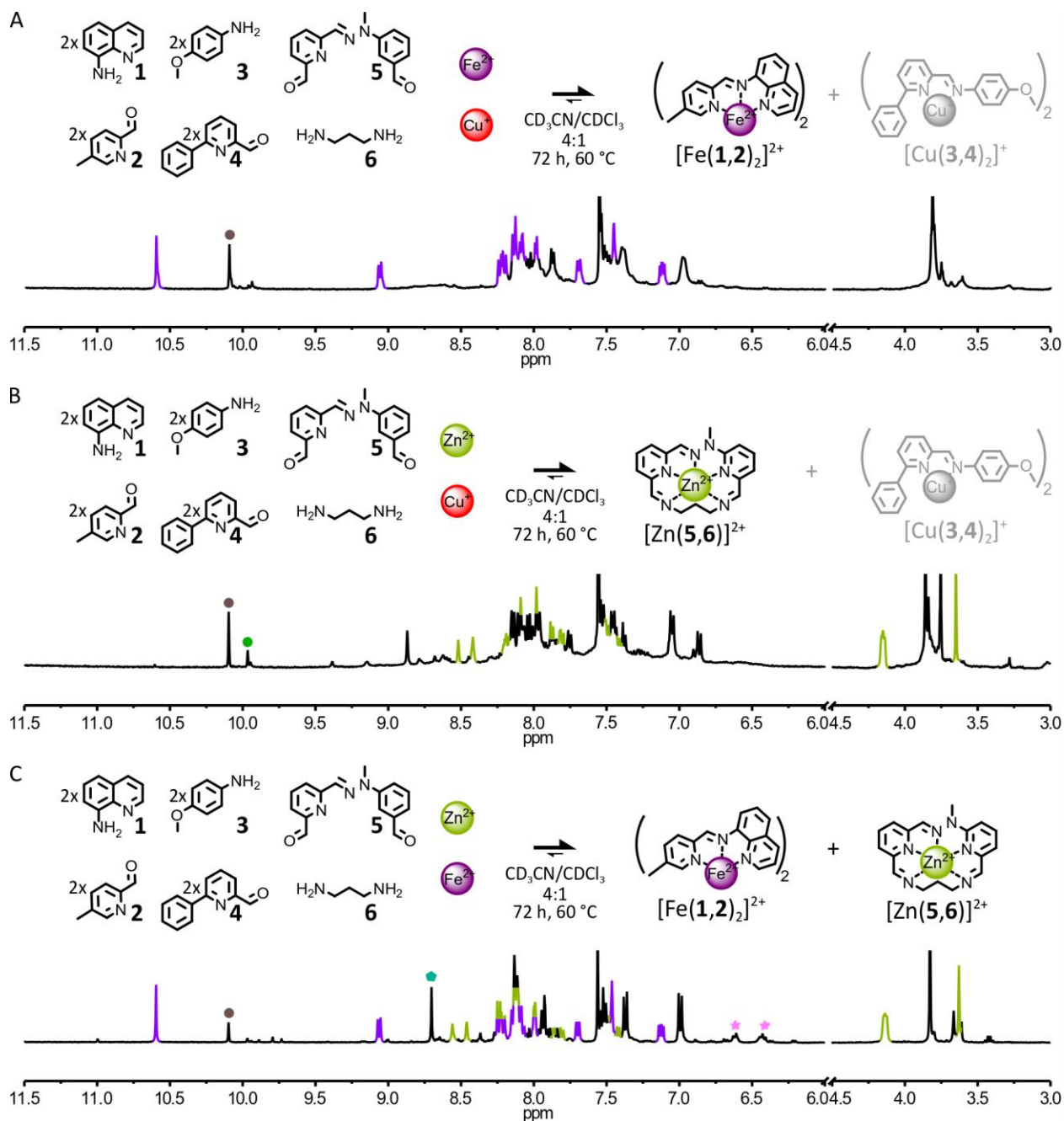
When the initial organic components were treated with 1 eq. of  $\text{Zn}(\text{BF}_4)_2$ , the affinity of the Zn(II) cations for the imine based macrocycle (**5,6**) was not strong enough to ensure the exclusive self-assembly of  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  (Figure 6C). After 3 days at 60 °C, about 55% of the initial Zn(II) ions were present as  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  and about 45% were present as  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$ .<sup>[14]</sup> The two complexes were observed alongside unreacted aldehyde **2** (about 45% of the initial amount), unreacted aldehyde **4**, (about 70% of the initial amount) and imine constituent (**3,4**) (which could not be precisely quantified due to overlap with other signals of unknown byproducts). The distribution of the Zn(II) cations between  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  matched closely that obtained when Zn(II) cations were added to a solution containing only components **1**, **2**, **5** and **6** (see results and discussion in section b.), suggesting that components **3** and **4** have no influence on the self-assembly of these two complexes.

#### ***e. Probing the synergistic behaviors during the self-assembly of the three complexes***

To probe the synergistic behaviour of the metal cations and to evaluate the influence of an additional third pair of organic components on the self-assembly process,  $\text{Fe}(\text{BF}_4)_2$ ,  $\text{Cu}(\text{BF}_4)$  and  $\text{Zn}(\text{BF}_4)_2$  were added in pairs (1 eq. each) to a solution of the components **1-6** in a 2:2:2:2:1:1 ratio in  $\text{CD}_3\text{CN}:\text{CDCl}_3$  (4:1). The resulting mixtures were heated at 60 °C for up to 3 days and the evolution of their composition was followed by  $^1\text{H}$  NMR spectroscopy.

When stoichiometric amounts of Fe(II) and Cu(I) salts were added to the solution of organic components (Figure 7A), the affinity of the Fe(II) cations for the imine constituent (**1,2**) was strong enough to allow the selective self-assembly of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ , 95% of the anticipated complex Fe(II) had formed after 3 days.<sup>[14]</sup> In contrast, the Cu(I) ions were not able to promote the formation of  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  despite the trapping of components **1** and **2** in  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$ . After 3 days, 65% of the initial component **4** was still unreacted. From this result, one can conclude that components **5** and **6** are likely to compete with components **3** and **4** for the formation of an alternative more stable Cu(I) or Cu(II) complex (unfortunately this alternative complex could not be identified).

When Zn(II) and Cu(I) salts were allowed to react with the initial library of components (Figure 7B), Cu(I) complex  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  was unable to self-sort from the reacting mixture (unfortunately no alternative copper complex could be identified). After 3 days, the only apparent complex in the  $^1\text{H}$  NMR spectrum of the reaction mixture was  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$ , accounting for 70% of the initial Zn(II) cations. The metallo-macrocycle was observed alongside unreacted aldehydes **2** (10% of the initial amount) and **4** (50%) and other unidentifiable species. No signals corresponding to the complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  could be detected in the  $^1\text{H}$  NMR spectrum of the reaction after 3 days or 6 days. In this case, the strong binding of aminoquinoline **1** to Cu(II) cations may explain both the absence of detectable Cu(I) complexes and the absence of the complex  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$ , aminoquinoline **1** is known to bind to Cu(I) cations and promote their oxidation to Cu(II).<sup>[9e]</sup>



**Figure 7.** (A) Upper – Attempted one-pot synthesis of the complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  through the self-sorting of their components from a mixture of components **1-6**. Only  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  was observed. Reaction conditions: **1:2:3:4:5:6:Fe**(BF<sub>4</sub>)<sub>2</sub>:Cu(BF<sub>4</sub>) (2:2:2:2:1:1:1:1), CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 60 °C, 72 h. Lower - Partial <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 298 K) of the crude reaction mixture after 72 h at 60 °C. The diagnostic signals of the complex  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  are colour coded in purple and one of the diagnostic signals of free aldehydes **4** are highlighted by a grey circle. (B) Upper – Attempted one-pot synthesis of the complexes  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Cu}(\mathbf{3},\mathbf{4})_2]^+$  through the self-sorting of their components **1-6**. Only  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  was observed. Reaction conditions: **1-6**, Fe(BF<sub>4</sub>)<sub>2</sub> and Cu(BF<sub>4</sub>) (2:2:2:2:1:1:1:1), CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 60 °C, 72 h. Lower - Partial <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub> 4:1, 298 K) of the crude reaction

mixture after 72 h at 60 °C. The diagnostic signals of the complex  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  are colour coded in green. (C) Upper – One-pot synthesis of the complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  through the self-sorting of its components from a mixture of components **1-6**. Reaction conditions: **1-6**,  $\text{Fe}(\text{BF}_4)_2$ ,  $\text{Zn}(\text{BF}_4)_2$  (2:2:2:2:1:1:1:1:1),  $\text{CD}_3\text{CN}:\text{CDCl}_3$  4:1, 60 °C, 72 h. Lower - Partial  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}:\text{CDCl}_3$  4:1, 298 K) of the crude reaction mixture after 72 h at 60 °C. The diagnostic signals of the complexes  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  and  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  are colour coded in green and purple, respectively, one of the diagnostic signals of free aldehydes **4** and **2** are highlighted by a grey circle and a green circle, respectively, one of the diagnostic signals of the imine-containing constituent (**3,4**) is highlighted by a turquoise pentagon and some of the diagnostic signals of aniline **3** are highlighted by pink stars.

The addition of a stoichiometric amount of Fe(II) and Zn(II) salts to the solution of the six organic components led to the near quantitative self-assembly of complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  (Figure 7C). 90% of the anticipated  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  complex and 98% of the anticipated  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  complex had formed after 3 days.<sup>[14]</sup> The lower percentage of  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  complex could be attributed to the presence of some residual Fe(II) heteroleptic complex  $[\text{Fe}(\mathbf{1},\mathbf{2})(\mathbf{1},\mathbf{4})]^{2+}$  involving 10% of the initial Fe(II) cations. The remaining components were found in the  $^1\text{H}$  NMR spectrum either as free components **1**, **3** and **4**, amounting to 5%, 25% and 25% of their initial amount, respectively, or as constituent (**3,4**), amounting for 70% of both initial components **3** and **4**. In the absence of components **3** and **4** complexes  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$  were unable to selectively self-assemble from their reactants due to the persistence of the kinetic product  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  in the reaction mixture even after 10 days at 60 °C. Here, after only 5 days at 60 °C no detectable amount of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  could be observed in the  $^1\text{H}$  NMR spectrum of the crude reaction mixture, indicating that the presence of components **3** and **4** must facilitate the rearrangement of  $[\text{Zn}(\mathbf{1},\mathbf{2})_2]^{2+}$  into  $[\text{Fe}(\mathbf{1},\mathbf{2})_2]^{2+}$  and  $[\text{Zn}(\mathbf{5},\mathbf{6})]^{2+}$ . After further investigations, it was found that the derivative of aniline **3** was the main contributor to the acceleration of the rearrangement (see the Supporting Information). However, the presence of both components **3** and **4** provided a cleaner outcome.

In a more general perspective, the reduction of the diversity of metal complexes formed upon addition of Fe(II) and Zn(II) cations to the library of six components **1-6** compared to their addition to the library of four components **1**, **2**, **5** and **6** (see results and discussion section c.) exemplifies the concept of “simplicity”,<sup>[9d-f]</sup> namely that an increase of the compositional complexity of a system (*i.e.* a larger number of components) may lead to a simplified output through dynamic competition.<sup>[9e]</sup>

## Conclusions

The above results demonstrate how the unique coordination preferences of Fe(II), Cu(I) and Zn(II) cations can be exploited to achieve the parallel self-assembly of three fully non-identical imine-containing metal complexes through the self-sorting of a library of six different amine- and 2-formylpyridine-containing components.

By selecting three metal complexes having a hierarchical ordering of their stability and by exploiting the regulatory relationships existing between the constituents of the CDN (*i.e.* antagonistic and agonistic relationships), it was possible to drastically reduce the amount of assembly instructions needed to achieved the selective self-assembly of the three different metal complexes. Only one of the three metal complexes needed to selectively self-assemble from the initial pool of reactants.

From the present study it appears important to not only considering the thermodynamic outcome of a self-sorting system when designing it but also to consider and aim to avoid kinetic traps that may appear during its assembling, as they may keep an ordered output out of reach. To this end, increasing the initial complexity of the system, by using a larger number of components, may facilitate the assembly process by accelerating the reorganization of some of these kinetic traps, resulting eventually in a simpler more ordered output (*i.e.* a smaller number of products).

The development of synthetic strategies to simultaneously control the outcome of multiple dynamic processes shared by several entities, is an indispensable step towards creating and exploiting complex dynamic networks of molecules rivalling in their complexity with biological systems.

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