



Cite this: *Chem. Sci.*, 2016, 7, 3689

Received 17th November 2015  
Accepted 3rd February 2016

DOI: 10.1039/c5sc04403k  
[www.rsc.org/chemicalscience](http://www.rsc.org/chemicalscience)

# Supramolecular reactions of metallo-architectures: $\text{Ag}_2$ -double-helicate/ $\text{Zn}_4$ -grid, $\text{Pb}_4$ -grid/ $\text{Zn}_4$ -grid interconversions, and $\text{Ag}_2$ -double-helicate fusion†

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Supramolecular reactions are of importance in many fields. We report herein three examples where complexes of hydrazone-based ligands are involved. A  $\text{Ag}_2$ -double-helicate was converted, by treatment with  $\text{Zn}(\text{OTf})_2$ , into a  $\text{Zn}_4$ -grid (exchange of metal ions and change of the nature of the initial complex). A  $\text{Pb}_4$ -grid was converted, upon reaction with  $\text{ZnCl}_2$  or  $\text{ZnBr}_2$ , into a  $\text{Zn}_4$ -grid (exchange of metal ions, but conservation of the nature of the initial complex). The reverse conversions were also achieved. The fusion of a  $\text{Ag}_2$ -double-helicate with another  $\text{Ag}_2$ -double-helicate was performed (exchange of ligands, but conservation of the nature of the complexes) and resulted in a mixture of three helicates (two homostranded ones and one heterostranded one).

## Introduction

Like covalent molecules, supramolecular<sup>1</sup> assemblies may participate in various reactions. The understanding of supramolecular reactions is of much interest because they are involved in many areas such as complex chemical systems and networks,<sup>2</sup> adaptive<sup>3</sup> and stimuli-responsive<sup>4</sup> chemical systems, fabrication of nanodevices and materials,<sup>4</sup> biomolecular processes. Thus, in the complexity and diversity of supramolecular chemistry, the reactivity of supramolecules plays a crucial role. It includes the processes:

(a) of (self)assembly (*i.e.* formation of supramolecular architectures through assembly, but also their participation, as subunits, in more complex assemblies), and correlatively, partial or total disassembly;

(b) of partial or total reorganization or exchange (at the supramolecular and, additionally and possibly, at the covalent level), that involves the breaking of several or all of the initial supramolecular connections and formation of new ones;

(c) without breaking or formation of new supramolecular connections (*e.g.* covalent modifications after self-assembly<sup>5</sup>).

Amongst supramolecular architectures, double helices and helicates,<sup>6</sup> as well as grids<sup>7</sup> arouse much interest and work. For example, DNA<sup>8</sup> and the ion channel generated by gramicidine<sup>9</sup>

have a double helical structure, and there are double helical complexes that act as molecular machines<sup>10</sup> or catalysts.<sup>11</sup> Grid-like complexes have been studied for their electrochemical and magnetic properties,<sup>7</sup> for their capacity to encapsulate ions<sup>12</sup> or as starting materials for building more complex architectures (*e.g.* a Solomon link<sup>13</sup>), amongst other things. However, supramolecular interconversions of grids and helicates have not, except several examples,<sup>14,15</sup> been much explored.

With these ideas in mind – and using principles such as the displacement of an equilibrium through precipitation, and the preference of  $\text{Ag}^+$  for tetrahedral and of  $\text{Zn}^{2+}$  for octahedral coordination – we designed, as reported herein, three supramolecular reactions<sup>16</sup> of reorganization and exchange (Fig. 1) involving grids and double helicates. They are related through the ligands<sup>17</sup> (which are pyrimidine-bis-hydrazones;<sup>18</sup> Fig. 2)

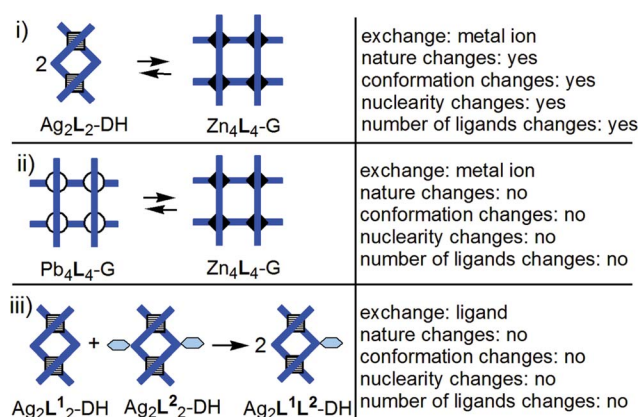


Fig. 1 Stylized representation of the three types of supramolecular reactions reported herein.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5sc04403k



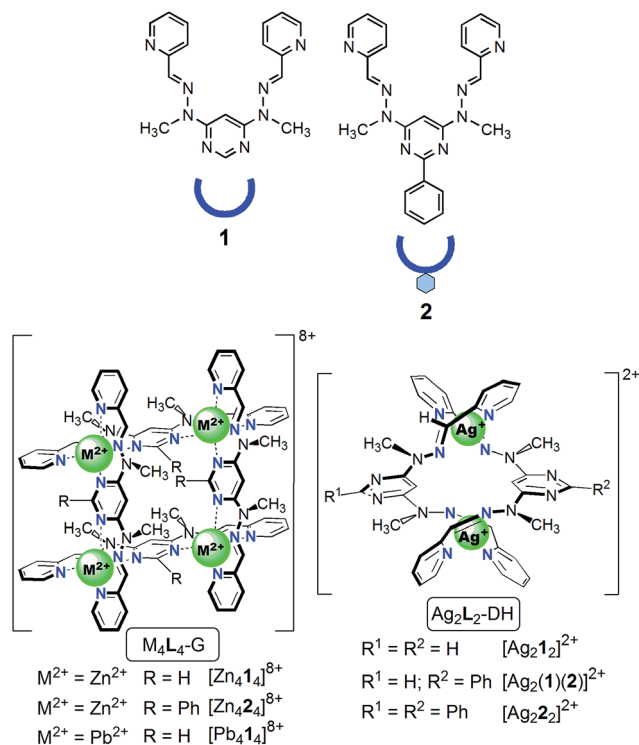


Fig. 2 Structural formulae and stylized representations of ligands 1 and 2, and of grids and double helicites.

that produce the supramolecular complexes, as well as through the nature of complexes, and occur due to the dynamic character of the present metal–ligand connections. These reactions (Fig. 1) can be seen as:

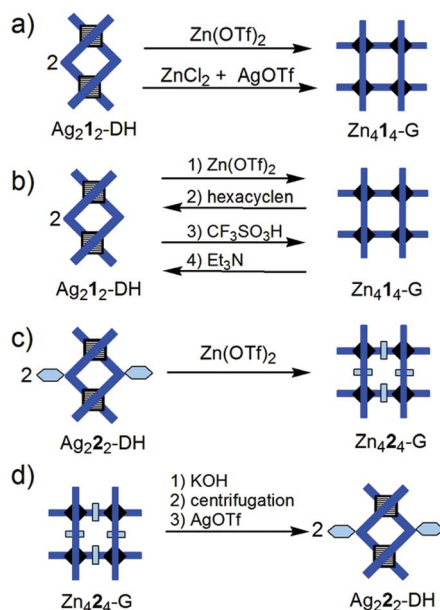


Fig. 3 Stylized representation of: (a) the conversion of  $Ag_21_2-DH$  double helicate into the  $Zn_41_4-G$  grid; (b) the interconversion  $Ag_21_2-DH/Zn_41_4-G$ ; (c) the conversion of  $Ag_22_2-DH$  double helicate into the  $Zn_42_4-G$  grid; (d) the conversion of  $Zn_42_4-G$  grid into  $Ag_22_2-DH$  double helicate. Charges and stoichiometric coefficients are omitted for simplicity.

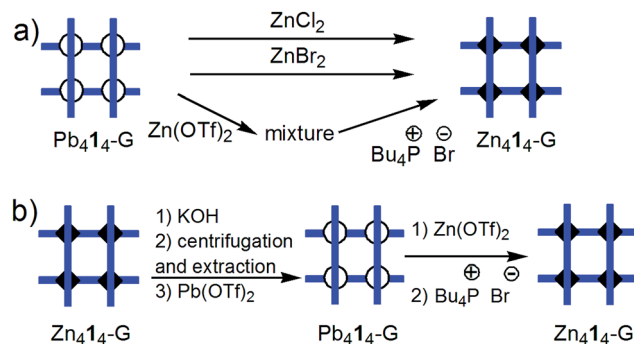


Fig. 4 Stylized representation of: (a) reaction of  $Pb_41_4-G$  grid with  $ZnCl_2$ ,  $ZnBr_2$ , and  $Zn(OTf)_2$  and  $Bu_4P^+Br^-$  (solvent  $CD_3CN$ ); (b)  $Zn_41_4-G/Pb_41_4-G$  and  $Pb_41_4-G/Zn_41_4-G$  conversions. Charges and stoichiometric coefficients are omitted for simplicity.

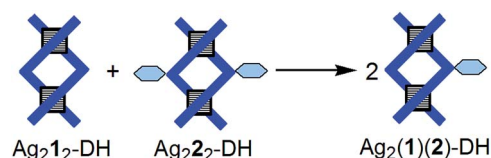


Fig. 5 Stylized representation of the fusion (conproportionation) reaction of double helicites  $Ag_21_2-DH$  and  $Ag_22_2-DH$  with formation of heterostrand species  $Ag_2(1)(2)-DH$ . Charges are omitted for simplicity.

(i) a change of the nature of the supramolecular architecture, from a  $Ag^+$  dinuclear double helicate (DH) into a  $Zn^{2+}$  tetranuclear grid (G), induced by replacement of  $Ag^+$  by  $Zn^{2+}$  (Fig. 3). In this reaction, not only the nature of the complex and that of the metal ion change, but also the conformation of the ligand (helical  $\rightarrow$  unfolded), the charge ( $2^+ \rightarrow 8^+$ ) and the nuclearity of the complex ( $2 \rightarrow 4$ ) and the number of ligands per complex ( $2 \rightarrow 4$ ). In regard to this last change, this process can be compared with the conversion or the equilibrium between supramolecular dimer and tetramer of bioactive proteins,<sup>19</sup> or between other homo-oligomers<sup>20</sup> with influence on the protein functions.

(ii) a substitution<sup>21</sup> (metal ion exchange or transmetallation), in a sole operation, of the four  $Pb^{2+}$  ions of a grid-like<sup>22</sup> complex by  $Zn^{2+}$  ions (Fig. 4);

(iii) a fusion (conproportionation)<sup>23</sup> between two  $Ag^+$  double helicites<sup>24</sup> (Fig. 5).

While in case (ii) the equilibrium is shifted towards the  $Zn^{2+}$  grid through the precipitation of  $Pb^{2+}$  as its halides (chloride and bromide), in cases (i) and (iii), the conversions can be done without precipitation.

## Results and discussion

(i) The conversion  $Ag_2L_2-DH \rightarrow Zn_4L_4-G$  ( $L = 1, 2$ ) through transmetallation is a dramatic reorganization of the nature of the metallo-supramolecular architecture induced by the replacement of  $Ag^+$  by  $Zn^{2+}$  (Fig. 3a and c):  $2 Ag_2L_2-DH + 4 Zn^{2+} \rightarrow Zn_4L_4-G + 4 Ag^+$ .  $Ag^+$  prefers a tetrahedral coordination geometry which is, in the case of ligands 1 and 2, achieved from 2 two-Nsp<sup>2</sup>-atom bidentate pyridine-hydrazone sites. In this



way,  $\text{Ag}^+$  induces the formation of double helicates with ligands **1** and **2**.  $\text{Zn}^{2+}$  prefers an octahedral coordination environment that results from **2** three- $\text{Nsp}^2$ -atom tridentate sites of type pyridine-hydrazone-pyrimidine, thus generating a grid.

Reaction of 1 equiv. of  $\text{Ag}_2\text{L}_2\text{-DH}^{15c}$  with 2 equiv. of  $\text{Zn}(\text{OTf})_2$  ( $\text{OTf}^- = \text{CF}_3\text{SO}_3^-$ ) produces – without the need to precipitate  $\text{Ag}^+$  as a halide – the corresponding grid  $\text{Zn}_4\text{L}_4\text{-G}^{15b,22a}$  (solvent:  $\text{CD}_3\text{NO}_2$  with 6–14%  $\text{CD}_3\text{CN}$ ; ESI, pp. S9–S11†). Where  $\text{ZnCl}_2$  is used in the reaction with  $\text{Ag}_2\text{L}_2\text{-DH}$ , two equivalents of  $\text{AgOTf}$  per equiv. of  $\text{DH}$  are required according to the equation (ESI p. S8†):



On treatment of the double helicate  $\text{Ag}_2\text{L}_2\text{-DH}$  in  $\text{CD}_3\text{NO}_2$  with 2 equiv. of  $\text{Zn}(\text{OTf})_2$  – added as a solution in a small volume of  $\text{CD}_3\text{CN}$ , or as a solid – the grid  $\text{Zn}_4\text{L}_4\text{-G}$  was obtained. When the double helicate  $\text{Ag}_2\text{L}_2\text{-DH}$  in  $\text{CD}_3\text{NO}_2$  was treated with 2 equiv. of  $\text{Zn}(\text{OTf})_2$ , added as a solution in a small volume of  $\text{CD}_3\text{CN}$  (about 6–14% of the  $\text{CD}_3\text{NO}_2$  volume), the grid  $\text{Zn}_4\text{L}_4\text{-G}$  was obtained. When  $\text{Zn}(\text{OTf})_2$  was added as a solid, without  $\text{CD}_3\text{CN}$ , was obtained a mixture without the  $\text{Zn}_4\text{L}_4\text{-G}$  grid; addition of a small volume of  $\text{CH}_3\text{CN}$  (about 6–14% of the  $\text{CD}_3\text{NO}_2$  volume) to this mixture produced the expected grid  $\text{Zn}_4\text{L}_4\text{-G}$ . A possible explanation could be that, in the case of the reaction  $\text{Ag}_2\text{L}_2\text{-DH} \rightarrow \text{Zn}_4\text{L}_4\text{-G}$ , the  $\text{CH}_3\text{CN}$  acts as a coordinating species for the  $\text{Ag}^+$  ions and so contributes to the displacement of the equilibrium from the double helix towards the grid. The grid  $\text{Zn}_4\text{L}_4\text{-G}$  should be – due to the  $\pi$ -stacking aromatic interaction between a phenyl ring and the two ligands between which that phenyl is located within the grid – more stable than the grid  $\text{Zn}_4\text{L}_4\text{-G}$ . This stability may be sufficient to make possible the formation of the grid  $\text{Zn}_4\text{L}_4\text{-G}$  from the corresponding double helicate without, unlike in the case of the grid  $\text{Zn}_4\text{L}_4\text{-G}$ , the assistance of  $\text{CH}_3\text{CN}$ .

DOSY NMR was also used to study the conversion  $\text{Ag}_2\text{L}_2\text{-DH} \rightarrow \text{Zn}_4\text{L}_4\text{-G}$  ( $\text{L} = \text{1, 2}$ ). As expected, the volume of the grid species obtained from double helicates on treatment with  $\text{Zn}(\text{OTf})_2$  was found in agreement with that of the grid prepared from the free ligands **L** and  $\text{Zn}(\text{OTf})_2$ .

The reverse conversion  $\text{Zn}_4\text{L}_4\text{-G} \rightarrow \text{Ag}_2\text{L}_2\text{-DH}$  can be done as follows: after treatment of the grid with  $\text{KOH}$ , the solvent ( $\text{CD}_3\text{CN}$  or  $\text{CD}_3\text{NO}_2$ ) is removed, and the ligand is extracted with  $\text{CDCl}_3$  and separated from the solid residue (by centrifugation or filtration); after removal of  $\text{CDCl}_3$ ,  $\text{CD}_3\text{NO}_2$  is added, then  $\text{AgOTf}$  is added to form the helicate. In order to simplify the procedure, we used ligand **2** and a mixture of  $\text{CDCl}_3$  and  $\text{CD}_3\text{NO}_2$  where ligand **2**, as well as the corresponding grid and double helicate were soluble. After precipitation of  $\text{Zn}^{2+}$  with  $\text{KOH}$ , the mixture was centrifuged (the ligand **2** being soluble in the mixture of solvents), and to the recovered liquid phase  $\text{AgOTf}$  was added to produce the  $\text{Ag}_2\text{L}_2\text{-DH}$  (ESI, p. S13†).

In a pH-dependent system (Fig. 3b), the interconversion between  $\text{Ag}_2\text{L}_2\text{-DH}$  and  $\text{Zn}_4\text{L}_4\text{-G}$  was achieved as follows (ESI, p. S10†): the grid was generated from the double helicate by reaction with  $\text{Zn}^{2+}$ ; then,  $\text{Zn}^{2+}$  was complexed with hexacyclen, and the double helicate was regenerated; partial protonation of

hexacyclen with  $\text{TfOH}$  caused release of  $\text{Zn}^{2+}$  and formation of the grid (incomplete yield); finally, addition of triethylamine reactivated the hexacyclen that again encapsulated  $\text{Zn}^{2+}$  and resulted in the reformation of the double helicate.

(ii) The  $\text{Pb}_4\text{L}_4\text{-G} \rightarrow \text{Zn}_4\text{L}_4\text{-G}$  conversion (Fig. 4a) can formally be seen as a substitution of  $\text{Pb}^{2+}$  by  $\text{Zn}^{2+}$  ions, although the real mechanism, involving breaking and formation of supramolecular bonds, must be more complex. Reaction of  $\text{Pb}_4\text{L}_4\text{-G}^{15b}$  with 4 equiv. of  $\text{Zn}(\text{OTf})_2$  produces a mixture which no longer contains the grid-like species  $\text{Pb}_4\text{L}_4\text{-G}$  or  $\text{Zn}_4\text{L}_4\text{-G}$  (ESI p. S2†). This suggests that the affinity of  $\text{Zn}^{2+}$  for the ligand, as well as its preference for octahedral coordination are not sufficient to displace the equilibrium towards  $\text{Zn}_4\text{L}_4\text{-G}$ . We considered that the involvement of  $\text{Pb}^{2+}$  ions in a weakly dissociating or sparingly soluble compound should displace the equilibrium. Indeed, addition of  $\text{Br}^-$  (as  $\text{Bu}_4\text{P}^+\text{Br}^-$ ) to the above mixture, or treatment of  $\text{Pb}_4\text{L}_4\text{-G}$  with four equivalents of  $\text{ZnBr}_2$  or  $\text{ZnCl}_2$  produced – along with the formation of  $\text{PbX}_2$  ( $\text{X} = \text{Br, Cl}$ ) which precipitates and, doing so, shifts the equilibrium – the expected  $\text{Zn}_4\text{L}_4\text{-G}$  grid (solvent:  $\text{CD}_3\text{CN}$ ; ESI pp. S3–S4†):  $\text{Pb}_4\text{L}_4\text{-G} + 4 \text{ZnX}_2 \rightarrow \text{Zn}_4\text{L}_4\text{-G} + 4 \text{PbX}_2$ .

The reverse conversion  $\text{Zn}_4\text{L}_4\text{-G} \rightarrow \text{Pb}_4\text{L}_4\text{-G}$  grid was achieved in several steps (Fig. 4b). Treatment of  $\text{Zn}_4\text{L}_4\text{-G}$  (in  $\text{CD}_3\text{CN}$ ) with  $\text{KOH}$  led to the precipitation of  $\text{Zn}^{2+}$  (as  $\text{Zn}(\text{OH})_2$  or  $\text{K}_2[\text{Zn}(\text{OH})_4]$ ), as well as of the free ligand **1**. After removal of  $\text{CD}_3\text{CN}$ , the free ligand **1** was extracted with  $\text{CDCl}_3$  and used further for the preparation of  $\text{Pb}_4\text{L}_4\text{-G}$  (see ESI, p. S5†).

Thus, in addition to its self-assembly from  $\text{Zn}^{2+}$  and a ligand, the same  $\text{Zn}^{2+}$  grid,  $\text{Zn}_4\text{L}_4\text{-G}$ , can be obtained, in reactions (i) and (ii), from a  $\text{Ag}^+$  dinuclear double helicate or from a  $\text{Pb}^{2+}$  tetranuclear grid (exchange of metal ions and reorganization of the architectures).

(iii) The fusion (conproportionation) reaction of double helicate  $\text{Ag}_2\text{L}_2\text{-DH}^{15c}$  with 1 equiv. of  $\text{Ag}_2\text{L}_2\text{-DH}$  (Fig. 5) according to the equation



produces a mixture that contains each of the three helicates, namely two homoleptic (homost stranded) ones and one heteroleptic (heterost stranded) one. Ligands **1** and **2** equally participate to homo- and heteroleptic helicates, and so the observed molar percentages are of approximately 25% for  $\text{Ag}_2\text{L}_2\text{-DH}$ , 25% for  $\text{Ag}_2\text{L}_2\text{-DH}$ , and 50% for  $\text{Ag}_2(\text{1})(\text{2})\text{-DH}$ . For characterization of the new compound  $\text{Ag}_2\text{L}_2\text{-DH}$ , see ESI pp. S14–S20;† for  $^1\text{H}$ ,  $^{13}\text{C}$  and DOSY of the mixture of three helicates, see ESI pp. S25–S31.†

For the reactions described above it might appear necessary, in practice, to slightly (2–10%) increase the amounts of reagents with respect to those theoretically calculated.

## Experimental

For experimental details, see the ESI.†

## Conclusions

To summarize, three supramolecular reactions were investigated: (i) a  $\text{Ag}_2\text{L}_2\text{-DH}$  double-helicate into  $\text{Zn}_4\text{L}_4\text{-G}$  grid



conversion, where the exchange of metal ions changes the nature of the metallo-supramolecular architecture, (ii) a  $\text{Zn}_4\text{14-G}$  grid into  $\text{Pb}_4\text{14-G}$  grid conversion driven by a halide-induced precipitation and where the nature of the metallo-supramolecular architecture is conserved, and (iii) a double exchange of ligands during the fusion of two double helicates.

The grid/grid and double-helicate/grid conversions were made reversible by precipitation of  $\text{Zn}^{2+}$  with KOH and subsequent reaction of the free ligand with  $\text{Ag}^+$  or  $\text{Pb}^{2+}$ , or, for one DH/G interconversion, in a pH-dependent way.

In perspective, such ligands could be introduced in larger and more complex, suitably decorated, architectures where such supramolecular reactions can act as actuators of various properties (charge, volume, multivalency).

## Acknowledgements

We thank Prof. Jack Harrowfield for helpful discussions, and Stéphanie Kouaho for mass spectrometry analyses.

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