## A fully dynamic five-component triangle via self-sorting<sup>†</sup>

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Clean fabrication of a five-component supramolecular triangle was elaborated *via* self-sorting. The robustness of the dynamic triangle against external stimuli was challenged by varying both the metal ions and their ratios. Self-sorting of five components proved to be superior to that of four components.

It is an important mission of supramolecular science to mimic the complexity and richness of biological self-assembly and self-organisation. Hence, the fabrication of multicomponent nano-assemblies has received considerable attention over the past years.<sup>1,2</sup> However, an increasing number of components not only opens a venue for growing emergent properties, but equally augments the intricacy of all competing interactions,<sup>3</sup> in such a way that supramolecular self-assembly of multiple building blocks into a single species becomes increasingly tricky. It thus comes as no surprise that the majority of all known metallo-supramolecular aggregates consists of just one type of ligand and one sort of metal ion, whereas architectures with multiple ligands ( $n \ge 2$ ) and multiple metal ions ( $n \ge 2$ ) are found to be scarce.

Nature artfully combines multiple components by means of self-sorting.<sup>4</sup> Thus, the transfer of connatural algorithms to artificial supramolecular species has received considerable attention over the past two decades.<sup>5-7</sup> Self-sorting in metallosupramolecular structures is managed by various factors, such as steric and electronic effects,  $\pi - \pi$  interactions, and metal-ion coordination specifics. After extensive optimisation, we have recently described a dynamic library comprising six different components (metal ions and ligands) and allowing for twenty different possibilities, from which only two metal complexes emerged (Scheme 1). As a proof of concept, the formation of a five-component (three ligands, two metal ions) supramolecular trapezoid was exemplified.<sup>6</sup> Herein, we report on the fabrication of the first five-component triangle by exploiting the above basis set of components in a different combination. The resultant isosceles triangular species proved to be robust while changing factors, such as excess, variation and ratio of metal ions.

Among all conceivable cyclic 2D nano-architectures, the triangle is the conceptually simplest supramolecular assembly and therefore its fabrication has initiated ample efforts.<sup>8</sup> Even though the common equilateral triangle has been studied *in extenso*, all other architectures (isosceles and scalene) are



Scheme 1 Self-sorting in a six-component library.

not yet realised well. To the best of our knowledge there is only a single report on self-assembled isosceles triangles,<sup>9</sup> realised through a combination of the HETTAP<sup>10</sup> and PHENLOCK<sup>11</sup> methodologies. While two different metal–ligand combinations were used, only one of them was truly dynamic, the other one was kinetically locked. Using exclusively dynamically exchanging components we present herein the fabrication of a fully supramolecular isosceles triangle, an architecture, which needs precise constitutional and positional control.

In order to establish the required positional control, we implemented the coordination motifs of 1-4 (Scheme 1) into the multitopic ligands 5–7 (Fig. 1), using a different combination as in ref. 6. The information contained in ligand 3 was implemented into the ditopic component 5, the latter being readily accessible by means of a Sonogashira cross-coupling reaction.<sup>12</sup> The coordination properties of ligands 1 and 4 were instated in the unsymmetrical bisphenanthroline 6, conveniently prepared *via* stepwise Sonogashira cross-coupling reactions (ESI†). The coordination features of ligands 2 and 4 were implemented in the terpyridine–phenanthroline hybrid 7, easily synthesised using a known procedure.<sup>6</sup> With the ditopic



Fig. 1 Ligands used in the current study.

Universitat Siegen - FB 8 (Chemie - Biologie), Adolf-Reichwein Str., Siegen D-57068, Germany. E-mail: schmittel@chemie.uni-siegen.de † Electronic supplementary information (ESI) available: Synthetic procedure and spectra for 6. DPV, <sup>1</sup>H-, <sup>13</sup>C- and DOSY-NMR spectra of T and ESI-MS of all relevant compounds. See DOI: 10.1039/ c0cc00191k



Scheme 2 Synthesis of the triangular assembly T (only *syn* diastereomer is shown).

ligands at hand, self-sorting was expected to lead to preferential formation of the  $[Zn(6_{phenAr2})(7_{terpy})]^{2+}$  subunit and consequential closure of the triangle T *via*  $[Cu(5)(7_{phen})]^{+}$  and  $[Cu(5)(6_{phen})]^{+}$  (Scheme 2).<sup>‡</sup>

In a first set of experiments, we combined the ligands 5, 6, 7 in an equimolar ratio in the presence of two equivalents of Cu<sup>+</sup> and one equivalent of Zn<sup>2+</sup> and refluxed the mixture in acetonitrile/ dichloromethane (3 : 1) for 3 h. After obtaining a clear red solution we characterised the reaction mixture using mass spectroscopy, <sup>1</sup>H and DOSY (diffusion-ordered spectroscopy) NMR, differential pulse voltammetry (DPV) and elemental analysis. The electrospray ionisation mass spectrum (ESI-MS) of the reaction mixture evidenced the clean formation of the triangular species  $\mathbf{T} = [Cu_2Zn(\mathbf{5})(\mathbf{6})(\mathbf{7})](OTf)_2(PF_6)_2$  (Scheme 2). In the accessible spectral region of m/z = 150-2000 only three intense peaks were observed, all of them corresponding to triangle T (Fig. 2). The most abundant peak at m/z = 685.8(four-charged) was assigned to  $[Cu_2Zn(5)(6)(7)]^{4+}$ , whereas the triply charged one at m/z = 963.7 was attributed to  $[Cu_2Zn(5)(6)(7)](OTf)^{3+}$ , and the doubly charged one at m/z = 1519.5 to  $[Cu_2Zn(5)(6)(7)](OTf)_2^{2+}$ .

To corroborate the clean self-assembly process we carefully interrogated the DOSY and <sup>1</sup>H NMR of **T**. As for the ESI-MS, both sets of data unambiguously supported the presence of only one species, *e.g.* the DOSY spectra showed only a single diffusion coefficient (ESI<sup>†</sup>). Additional information could be derived from the <sup>1</sup>H NMR signals of the methoxy protons, as they appear in a diagnostic region. In **T**, eight singlets are expected for the four methoxy groups due to their



Fig. 2 ESI-MS of the triangle T in acetonitrile along with its isotopic distribution (black: experimental; red: calculated for  $[Cu_2Zn(5)(6)(7)]^{4+}$ ).



**Fig. 3** Partial <sup>1</sup>H NMR (400 MHz, 298 K, CD<sub>3</sub>CN) spectra of an equimolar mixture of **5**, **6**, **7** in the presence of (a) 3 equivalents of Cu<sup>+</sup>, (b) 3 equivalents of Zn<sup>2+</sup> and (c) 3 equivalents of a Cu<sup>+</sup> and Zn<sup>2+</sup> (2 : 1) metal salt mixture.

constitutional difference in the chiral heteroleptic copper(1) complex  $[Cu(6)(7)]^+$  and due to the occurrence of two diastereomers.<sup>13</sup> The <sup>1</sup>H NMR of the assembly indeed showed eight singlets between 2.73-3.06 ppm (Fig. 3c). Integration of the two sets of singlets allowed us to determine the ratio of the diastereomers as approximately 3 : 2. As ligand 7 can connect via the terpyridine or phenanthroline unit to 6, thus involving either  $[M(\mathbf{6}_{phenAr2})(7_{terpy})]^{n+}$  or  $[M(\mathbf{6}_{phenAr2})(7_{phen})]^{n+}$ linkages,<sup>‡</sup> verifying the correct connectivity of ligands 5-7 in the triangular assembly requires special attention. Comparison of the proton resonances of T with those of  $[M(phenAr_2)(phen)]^{n+1}$ or  $[M(phenAr_2)(terpy)]^{n+}$ , units from similar compounds, provides convincing evidence that 7 is connected to 6 via the  $[M(6_{phenAr2})(7_{terpy})]^{n+}$  unit. For example, in a rectangle serving as a reference,<sup>6</sup> the methoxy protons appear at 3.19–3.39 ppm for  $[M(phenAr_2)(phen)]^{n+}$  while they arise at 2.68–2.82 ppm for  $[M(phenAr_2)(terpy)]^{n+}$  moiety. Similarly, the proton resonances for methoxy groups arise at 2.71-2.85 ppm for the  $[M(phenAr_2)(terpy)]^{n+}$  unit in a supramolecular isosceles trapezoid.<sup>6</sup> As the MeO proton resonances in T show up at 2.73-3.06 ppm, they point to the occurrence of a  $[M(phenAr_2)(terpy)]^{n+}$  unit while ruling out the existence of a  $[M(phenAr_2)(phen)]^{n+}$  complex. Thus, self-assembly occurs in full agreement with the strategy conceived on the basis of our model compounds (Scheme 1).

DPV is a good tool to characterise supramolecular species with redox active subunits. The knowledge that copper(1) ions show distinct oxidation potentials in combination with ligands 1-4 allows to analyse for the presence of different copper(1) centres in T. In the mononuclear complex  $[Cu(1)(4)](PF_6)$  the copper(I) oxidation wave is observed at +0.29 V<sub>SCE</sub>, whereas for  $[Cu(3)(4)](PF_6)$  and  $[Cu(1)(2)](PF_6)$  the oxidation is seen at +0.44 V<sub>SCE</sub> and -0.21 V<sub>SCE</sub>, respectively.<sup>6</sup> For T, only one type of copper(I) complex is expected, but the presence of two diastereomers may lead to two closely spaced oxidation waves. Indeed, deconvolution of the broad peak at  $0.62 V_{SCE}$  revealed oxidation waves (Fig. 4) at 0.59 and 0.64  $V_{SCE}$  in a ratio of to ca. 3 : 2, which agrees well with the diastereomer ratio detected in the <sup>1</sup>H NMR. The oxidation values agreed well with those found in similar copper(1) complexes, as for example in a supramolecular trapezoid with 0.61 and 0.67 V<sub>SCE</sub>.<sup>6</sup>



**Fig. 4** Differential pulse voltammogram of **T** in acetonitrile with 0.1 M  $nBu_4NPF_6$  as electrolyte against a Ag wire used as a quasireference electrode and 1,1'-dimethylferrocene (left wave) as internal standard (scan rate of 20 mV s<sup>-1</sup> and a pulse height of 2 mV).

The latter observation also unambiguously validated the location of the metal ions inside the triangle **T**, as absence of any peak at negative potential excluded the possibility of a  $[Cu(phenAr_2)(terpy)]^+$  unit.‡ Thus **7** is coordinated to **6** *via* a  $[Zn(phenAr_2)(terpy)]^{2+}$  complex, while the remaining corners are occupied by Cu<sup>+</sup> metal ions (Scheme 2).

From the above experiments and analytical data the exclusive formation of the triangular assembly T is proven to arise from a combination of three different ligands in the presence of three equivalents of metal ions (one equiv. of  $Zn^{2+}$ ions and two equiv. of Cu<sup>+</sup> ions). One may, however, argue that it is the potentially cooperative binding in the cyclic ligand array of T that drives self-assembly in the presence of any metal ions. We thus prepared the triangular assemblies using either exclusively Zn<sup>2+</sup> or Cu<sup>+</sup> ions. ESI-MS data confirmed the formation of the triangular  $[M_3(5)(6)(7)]^{n+}$  assemblies (ESI<sup>†</sup>; Fig. S8 and S9). However, the <sup>1</sup>H spectra of the homometallic triangles  $[M_3(5)(6)(7)]^{n+}$  (Fig. 3a and b) appear much more complicated than that of the heterometallic case (Fig. 3c). A comparison of all <sup>1</sup>H NMR spectra clearly shows that the number of signals for methoxy groups and thus of constitutional isomers increases in case of homometallic scenarios. To demonstrate this case, we reacted the homometallic triangle  $[Cu_3(5)(6)(7)](PF_6)_3$  with one equivalent of  $Zn^{2+}$  and kept it at reflux for 3 h. The colour faded from dark red to light red and the <sup>1</sup>H NMR became akin to that observed for  $\mathbf{T} = [Cu_2Zn(5)(6)(7)](OTf)_2(PF_6)_2 (ESI^{\dagger}; Fig. S6).$ 

The observations can be rationalised in the following way. For the homometallic copper(1) or zinc(11) self-assembly, the ligands organise into differently connected triangular arrays. As the connection of ligands 5 and 6 is firmly instated, the terpyridine part of 7 may connect with either 5 or 6 leading to two dissimilar triangular species. On the contrary, in the mixed metal scenario the terpyridine of 7 has to connect with 6, as demonstrated in Scheme 1. Thus, the self-assembly process clears up through self-sorting. Interestingly, due to the beauty of self-sorting the five-component assembly (five different starting materials, mixed metal scenario) was flawless as compared to the four-component assembly (see the homometallic triangles). Moreover, the homometallic triangle  $[Cu_3(5)(6)(7)](PF_6)_3$  was easily converted into the heterobimetallic T simply by adding one equivalent of  $Zn^{2+}$ , lending extra proof for the dynamic nature of all triangles  $[M_3(5)(6)(7)]^{n+}$ .

In conclusion, we have described the clean formation of the five-component triangular species **T**. The structure was established by ESI-MS, <sup>1</sup>H NMR, DOSY, DPV and elemental analysis. Self-sorting was interrogated in the presence of different metal ion scenarios. Importantly, self-sorting does not only lead to **T** when all components are applied in a stoichiometric manner, but equally when excess amounts of the required metal ions are available. The latter aspect may become important for repairing defect metal ion corners in **T**, and thus is reminiscent of biological multi-component assemblies being in exchange with their surrounding. Moreover, self-sorting also led to ligand reorientation inside the supramolecular assembly, a switching process possibly of use for the fabrication of complex molecular machines.<sup>14</sup>

## Notes and references

 $\ddagger$  phen = [1,10]phenanthroline; phenAr<sub>2</sub> = 2,9-bis(2,6-dimethoxy-phenyl)-3-ethynyl-[1,10]-phenanthroline; terpy = [2,2';6',2'']terpyridine.

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