From an Eight-Component Self-Sorting Algorithm to a Trisheterometallic Scalene Triangle

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Abstract: Using motifs from *3-fold completive* self-sorting in an eight-component library, we report on the design and fabrication of a fully dynamic trisheterometallic scalene triangle, a demanding supramolecular structure that complements the so far known triangular structures.

To fit with the trend of evolution ("*Evolutionary processes are anamorphic, or complexity-generating*"),[1] artificial self-assembly will need to master vastly enhanced complexity and diversity issues, for example by enlarging the number of different components and interactions.[2] While biological self-assembly follows intricate orthogonal self-sorting algorithms,[3-5] artificial self-sorting is still limited in orthogonality. Indeed, most of the known self-sorting processes entail either multiple species or a single assembly along with excess ligand(s).[3-5] In contrast, we seek to merge all members of a library in a single multicomponent aggregate employing *completive*[5] and *integrative*[4] self-sorting. As an example we elaborated the self-assembly of a dynamic bimetallic trapezoid from a six-component $A^1A^2D^1D^2D^3D^4$ (A = acceptor, D = donor) library.[5] Extending the above conceptual insights to self-sorting in an eight-component $A^1A^2A^3D^1D^2D^3D^4D^5$ library (Scheme 1), we report herein on the fabrication of a trisheterometallic scalene triangle, a demanding and until now unrealized supramolecular structure (Scheme 2) that complements the so far known triangles (monometallic and equilateral,[6] bisheterometallic,[7,8] and isosceles[9,10]).

Self-sorting in metallosupramolecular structures is managed by various factors, such as steric and electronic effects, $\pi-\pi$ interactions, and metal-ion coordination specifics. For the self-sorting eight-component library depicted in Scheme 1, we chose to blend our previous $A^1A^2D^1D^2D^3D^4$ library[5] with the pyridine−zinc porphyrin binding motif.[11] To our delight, full orthogonality of the pyridine−zinc porphyrin binding motif with the two other individual heteroleptic metal−ligand combinations was established. Only 3

Scheme 1. Self-Sorting in a $A^1A^2A^3D^1D^2D^3D^4D^5$ Library
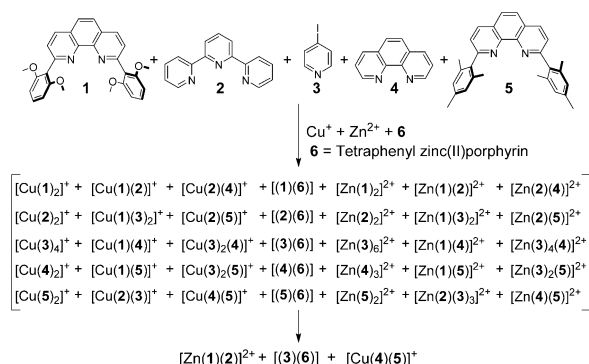
Scheme 2. Synthesis of the Supramolecular Scalene Triangles T_n
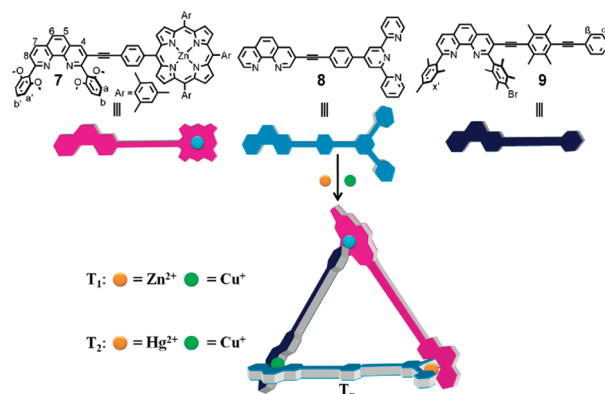
out of 35 plausible combinations, *i.e.* $[Zn(1)(2)]^{2+}$, $[Cu(4)(5)]^+$, and $[(3)(6)]$, were afforded while making full use of all library members in a *3-fold completive* self-sorting (readily derived from ^{1}H NMR analysis; see Supporting Information). Obviously, none of the available bi- or tridentate ligands can amalgamate readily with the zinc porphyrin **6** due to steric bulk, all the more as this would lead to uncoordinated nitrogen ligands in the overall mixture, which would violate the maximum site occupancy rule.[3a]

With the complexes $[Zn(1)(2)]^{2+}$, $[Cu(4)(5)]^+$, and $[(3)(6)]$ representing the three corners of a scalene triangle, all tools are available for designing the three different sides along with their binding units (Scheme 2). Thus, we instated **1** and **6** as the termini of the phenanthroline−porphyrin hybrid **7** being readily accessible *via* Sonogashira cross-coupling (Supporting Information). Along a known procedure,[5] **2** and **4** were merged in the terpyridine−phenanthroline ligand **8**, while the complexation properties of **3** and **5** were amalgamated within the phenanthroline−pyridine hybrid **9**. Details of the synthesis are contained in the Supporting Information. For all ligands, spacers were chosen to render the building blocks **7**−**9** unequal in length.

In a first set of experiments all components (**7**, **8**, **9**, Zn^{2+}, and Cu^+) were mixed in 1:1:1:1:1 ratio and refluxed for 2 h in acetonitrile/DCM (2:1). After obtaining a clear dark-violet solution the reaction mixture was characterized by electrospray ionization mass spectroscopy (ESI-MS), ^{1}H NMR, COSY, diffusion-ordered spectroscopy (DOSY), elemental analysis, and differential pulse voltammetry (DPV). ESI mass spectra (Figure 1) showed only peaks that were in full agreement with $T_1 = [CuZn(7)(8)(9)](OTf)_2(PF_6)$. Most importantly, the full integrity of the scalene triangle T_1 was unambiguously proven by intense signals at $m/z = 894.9$, associated with $[CuZn(7)(8)(9)]^{3+}$ and at $m/z = 1415.5$, associated with $[CuZn(7)(8)(9)](PF_6)^{2+}$.

Data from ^{1}H NMR and DOSY NMR (Supporting Information) further supported the structural assignment of T_1. A single diffusion
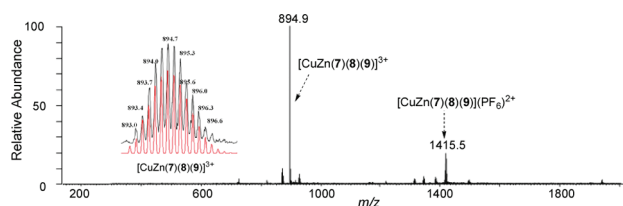
Figure 1. ESI-MS of the scalene triangle T_1. Inset: Experimental (black line) and calculated (red line) isotopic distribution of $[CuZn(7)(8)(9)]^{3+}$.

coefficient as well as a single set of signals provided evidence for the clean formation of the scalene triangle T_1 in solution. In order to evaluate the connectivity of the ligands in T_1 we paid special attention to several characteristic proton resonances. For example, the pyridine protons (α, β) of **9** in T_1 experienced a diagnostic upfield shift from 8.61 to 2.62 ppm and from 7.38 to 5.66 ppm in the ^{1}H NMR, respectively, a typical shift of pyridine protons upon axial coordination to a zinc porphyrin.[11] Thus, following our design, ligand **7** is indeed connected to **9** by a zinc porphyrin−pyridine interaction (Scheme 2). Diagnostically shifted b-H, b′-H protons of **7** yielded further information regarding the connectivity in T_1. The ca. 0.60 ppm upfield shifts of b-H and b′-H protons (from 7.40 and 7.50 ppm in **7** to 6.78 and 6.95 ppm in T_1) are indicative of a $[Zn(7_{phenAr2})(8_{terpy})]^{2+}$ complex.[5,12]

The suggested structure requires that T_1 is chiral due to the stereogenic $[Cu(8_{phen})(9_{phenAr2})]^+$ unit. As a result, several groups being homo- or enantiotopic in the individual ligands become diastereotopic in T_1. For example, the four methoxy groups of **7** show up as four singlets at 2.85−2.93 ppm. Their shift is indicative of a $[Zn(7_{phenAr2})(8_{terpy})]^{2+}$ complex.[5] Likewise, the two mesityl protons (x′) become diastereotopic in T_1 (δ = 5.92, 6.10 ppm). As these protons show up at δ = 6.92 ppm in **9**, their characteristic upfield shift in T_1 confirms the $[Cu(8_{phen})(9_{phenAr2})]^+$ complexation.[7]

The assortment of the metal ions in the two metal exchanging corners of the scalene triangle was interrogated by DPV probing the Cu$^+$ oxidation wave. Due to the diagnostically different redox potentials of $[Cu(4)(5)]^+$ ($E_{1/2}$ = 0.44 V_{SCE}), $[Cu(1)(4)]^+$ (0.29 V_{SCE}) and $[Cu(1)(2)]^+$ (−0.21 V_{SCE}),[5] a mixture of copper(I) complexes would show several copper(I) oxidation waves. A single oxidation wave at 0.76 V_{SCE} in T_1 (Supporting Information) confirmed the presence of only one type of copper(I) complex, pointing persuasively to the formation of $[Cu(8_{phen})(9_{phenAr2})]^+$. A combination of ESI-MS, ^{1}H NMR, DPV, DOSY, and elemental analysis thus unambiguously provided evidence for the clean formation of scalene triangle T_1.

Despite the many different entities potentially arising from five donor and three acceptor units, the exclusive formation of T_1 based on thermodynamic equilibration is no surprise in light of the *3-fold completive self-sorting* described in Scheme 1 and the design criteria applied to ligands **7**−**9**. Thus, it seems to be a promising strategy for future multicomponent structure design to first probe *completive* self-sorting in a library of mononuclear cornerstones and then to merge the motifs in multiligand building blocks for *integrative* self-sorting.

In another experiment, we replaced Zn^{2+} by Hg^{2+} following a similar protocol to fabricate the trimetallic scalene triangle T_2. **7**, **8**, **9**, Hg^{2+}, and Cu$^+$ were mixed in a 1:1:1:1:1 ratio and refluxed for 2 h in acetonitrile/DCM = 2:1. As for T_1, ^{1}H NMR and ESI-MS data supported the clean formation of the trisheterometallic scalene triangle T_2. As Hg^{2+} binds more strongly than Zn^{2+} in $[M(terpy)(phenAr2)]^{n+}$ complexes,[13] we tested metal exchange in T_1 upon addition of Hg^{2+} (1 equiv). Complete transformation of T_1 to T_2 was noticed within one day as evidenced from ESI-MS.
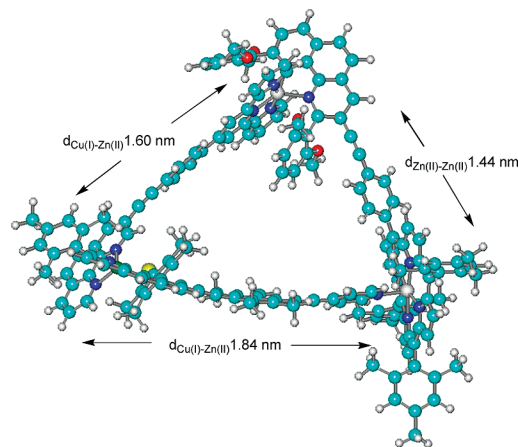

Figure 2. Energy minimized structure of the scalene triangle T_1. Counteranions are not included.

As all attempts to obtain a crystal structure of T_n were met with failure, MM$^+$ force field computations and molecular dynamics on T_n provided some insight about their structure as scalene triangles. Taking the metal−metal distance as a measure, the three metal corners of T_1 are separated by 1.44, 1.60, and 1.84 nm in the energy minimized structure (Figure 2) and by 1.44, 1.66, and 1.84 nm in T_2 (Supporting Information), nicely illustrating the geometrical scalene arrangement of T_n.

In conclusion, we report on the fabrication of two scalene triangles T_n that were designed along the eight components of a *3-fold completive* self-sorting library. The triangles are scalene from both a geometrical and a compositional point of view. Precise tuning of steric and electronic effects, $\pi-\pi$ interactions, and metal-ion specifics led to the formation of a single species in solution excluding other aggregates. To the best of our knowledge, T_1 and T_2 are the first supramolecular scalene triangles with three different self-assembled corners. Furthermore, T_2 is the first trisheterometallic scalene triangle. Such structural diversity in a rather simple supramolecular architecture points the way to promising devices with electronically different subunits.[14]

Supporting Information Available: Experimental procedures and spectroscopic data are provided for **7**, **9**, and all triangular assemblies T_n. This material is available free of charge via the Internet at http://pubs.acs.org.

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