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Multicomponent Assembly of Heterometallic Isosceles Triangles

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The multicomponent synthesis and solution-state characterization of three supramolecular bis-heterometallic isosceles triangles are elaborated. The triangular assemblies are isosceles both geometrically and chemically; they comprise multiple ligands, metals, and binding motifs. Variation of the length of one side of the triangle by changing the number of phenyl spacers $n = 0$, 1, and 2 influences the redox potential of the opposing copper(I) center, allowing translation of the nanomechanical changes into electronically readable values.

Over the last 2 decades, the design and fabrication of supramolecular nanoarchitectures using self-assembly have received considerable attention.[1] Among the various noncovalent binding tools to build intricate assemblies, metal coordination has turned out to be one of the most successful protocols. Even multifaceted construction algorithms can easily be stored as information in the metal centers and molecular components, allowing reliable readout of the encoded instructions. Thus, metallosupramolecular approaches have been utilized to forge a large assortment of fascinating two- and three-dimensional nanoarchitectures.[1] The majority thereof, however, is comprised of only two different components and a single binding motif. This limitation suggests the need to explore ways to increase complexity and diversity,[2] particularly as higher-order multicomponent architectures[2b] using coordination-driven self-assembly remain rare.[3−6]

The deficiencies and limitations of the presently used metal-coordination toolkits are so pronounced that even the clean preparation of a supramolecular triangle, formally the simplest and smallest member of the two-dimensional family of macrocycles, has been generating immense problems. Typically, supramolecular triangles show up in equilibrium with larger aggregates, such as squares or other polygons,[7] so that only in very few cases exclusive formation of the triangle was ascertained.[8,9] Furthermore, the reported triangles so far are usually homometallic as well as equilateral, both geometrically and chemically (Figure 1a).[10] In the following, we will demonstrate that the until now unknown geometrically and chemically isosceles supramolecular triangles (Figure 1d) can be prepared in a clean heterometallic form. This progress is a promising step toward the geometrically and chemically scalene triangle (Figure 1e), the holy grail of supramolecular triangles.

To overcome the problems associated with angular compression at acute angles, an increased challenge for geo-

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(10) Definitions: a chemically equilateral triangle is a triangle with the same ligand; a geometrically equilateral triangle is a triangle with sides of the same length.

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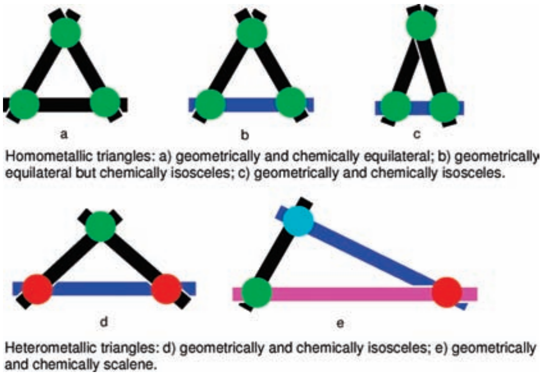


Figure 1. Cartoon representation of different types of triangles, both homo- and heterometallic.

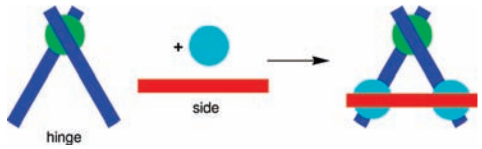
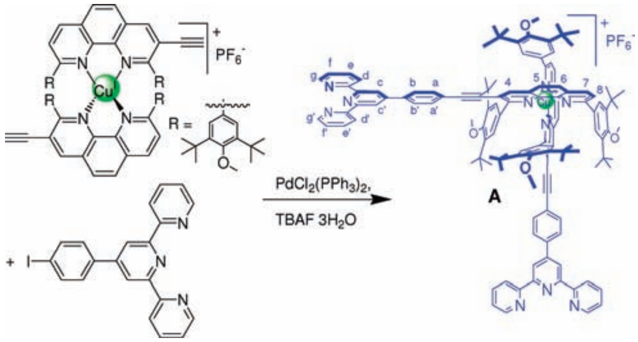
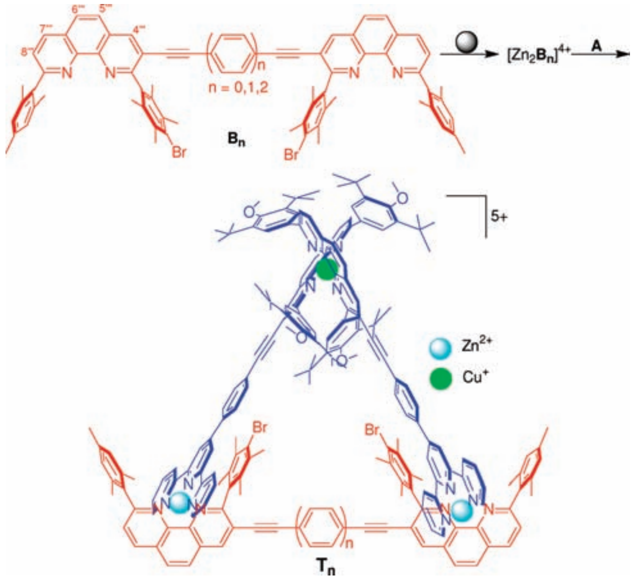


Figure 2. Cartoon representation of the self-assembly. A kinetically locked angular hinge is reacted in a metallosupramolecular heteroleptic aggregation with the third side.

Scheme 1. Synthesis of Angular Complex **A**



Scheme 2. Self-Assembly of Isosceles Triangles $\mathbf{T}_n$



metrically isosceles supramolecular triangles (Figure 1c,d), we used benefits from entropy and heteroleptic aggregation as provided by the PHENLOCK[11] and HETTAP[12] protocols. The PHENLOCK concept allows the preparation of a kinetically locked copper(I) bis(phenanthroline) complex[11] that is useful as a moderately flexible hinge unit (Figure 2). The combination of the latter with a third side through heteroleptic aggregation along the HETTAP[13] concept leads to the desired geometrically and chemically isosceles triangles. In addition, the use of C_s-symmetric HETTAP complex units also precludes the formation of diastereomers as received in our earlier work on geometrically equilateral triangles.[9] Thus, the chiral hinge **A** (Scheme 1) containing a kinetically locked copper(I) bis(phenanthroline) complex and two terpyridine terminals was conceived. Its amalgamation with ligand $\mathbf{B}_n$[14] opens a direct venue to a variety of isosceles triangles $\mathbf{T}_n$ ($n = 0$, 1, and 2; Scheme 2).

Synthesis of hinge **A**, similar to an analogous hinge with phenanthroline terminals, was realized.[9] First, a kinetically locked bis(phenanthroline)copper(I) complex functionalized with alkynes was prepared that was further equipped in a Sonogashira coupling with two terpyridine terminals. Fabrication of the isosceles triangles $\mathbf{T}_n$ was carried out by adding **A** to an acetonitrile solution of bisphenanthroline $\mathbf{B}_n$ and Zn^{2+} at 60 °C for 2 h. In another set of experiments, all components were taken up together in acetonitrile, refluxing the solution for 6 h. Exclusive formation of the isosceles triangle $\mathbf{T}_n$ was confirmed in both cases. In the latter case, we initially observed the formation of $\mathbf{T}_n$ along with a homoleptic complex of **A** (mainly $[Zn_2(\mathbf{A})_2]^{6+}$), but with elapsed time, self-repair occurred, leading to the exclusive formation of $\mathbf{T}_n$. Because of the required self-correction, the reaction time was longer. Each triangle $\mathbf{T}_n$ ($n = 0$, 1, and 2) was characterized by clean electrospray ionization mass spectra (ESI-MS), showing exclusively signals of the expected triangle (Figure 3, top, and the Supporting Information), ^{1}H and ^{13}C NMR, and elemental analysis.

^{1}H NMR data nicely support the formation of the triangles $\mathbf{T}_n$. The upfield shifts of the mesityl protons (Figure 3, bottom; $\delta \approx 7.0$ ppm in ligand $\mathbf{B}_n$, $\delta \approx 6.2$ ppm in triangle $\mathbf{T}_n$) are most diagnostic for heteroleptic complex formation as established earlier.[12] Likewise, because of the strong shielding effect of the bisphenanthrolines $\mathbf{B}_n$, the α protons (g, g′) of the terpyridine unit in $\mathbf{T}_n$ experienced a notable upfield shift. Downfield shifts of the 4‴ and 7‴ protons in the phenanthroline units of $\mathbf{B}_n$ are also clearly indicative of the self-assembled triangular structure.

The single phenanthroline-proton set is clear evidence for the existence of just one single triangle in solution; no isomeric species were detectable in variable-temperature NMR (+25 to −25 °C; see the Supporting Information).

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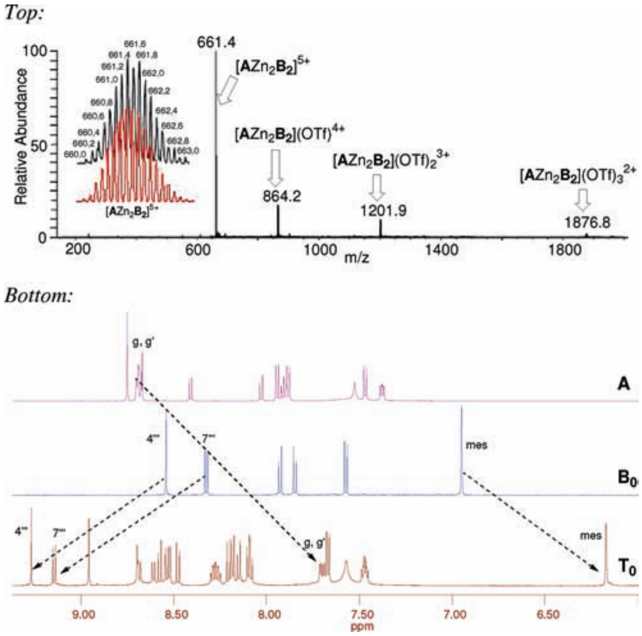

Figure 3. Top: ESI-MS spectrum of $\mathbf{T_2}$ in acetonitrile. Bottom: Partial ^{1}H NMR (600 MHz, 298 K) spectra of **A** (CD_2Cl_2), $\mathbf{B_0}$ (CD_2Cl_2), and $\mathbf{T_0}$ (CD_3CN).

Because of the stereogenic unit in **A**, protons of the terpyridine units and the aromatic substituents of bisphenanthroline are expected to be diastereotopic in $\mathbf{T}_n$. Indeed, this could be confirmed by ^{1}H NMR, with all assignments being verified by COSY spectra.

Variations in the length of the bisphenanthroline $\mathbf{B}_n$ are expected to cause either a change in the geometry near the metal centers and/or a bending in the ethynyl moieties. In fact, ^{1}H NMR data hint that both processes play a role. Because of the reduced steric bulk at the two zinc(II) centers, their geometric adjustment is more pronounced, as evinced from the large chemical shift changes of the surrounding protons. On the other hand, chemical shifts are affected less near the kinetically inert copper(I) center in $\mathbf{T}_n$ as a function of $n = 0$, 1, and 2. Changes in the chemical shifts at the aromatic spacer in $\mathbf{T_1}$ and $\mathbf{T_2}$ suggest some bending near the ethynyl moieties. Changes in the ^{13}C NMR resonance of the ethynyl carbons [$\delta(\mathbf{T_0}) = 90.9$ and 98.1 ppm; $\delta(\mathbf{T_1}) = 90.4$ and 98.4 ppm; $\delta(\mathbf{T_2}) = 90.5$ and 99.9 ppm for the ethynyl groups near the copper(I) center] also support this view.

To have further insight into the geometry of the isosceles triangles, solid-state structures would certainly be desirable. Unfortunately, all efforts directed toward the generation of single crystals suitable for X-ray analysis proved to be unsuccessful. Alternatively, we performed MM$^+$ computations, providing $Zn^{II}-Cu^{I}$ and $Zn^{II}-Zn^{II}$ distances of 1.59 and 1.28 nm, respectively, for the energy-minimized structure of $\mathbf{T_0}$ (Figure 4). In combination with the numbers (Supporting Information) for $\mathbf{T_1}$ ($d_{Zn^{II}-Cu^{I}} = 1.61$ nm; $d_{Zn^{II}-Zn^{II}} = 1.61$ nm) and $\mathbf{T_2}$ ($d_{Zn^{II}-Cu^{I}} = 1.62$ nm; $d_{Zn^{II}-Zn^{II}} = 1.94$ nm), a trend becomes apparent: the angular complex **A** in $\mathbf{T}_n$ ($n = 0$, 1, and 2) is increasingly bent with smaller n.

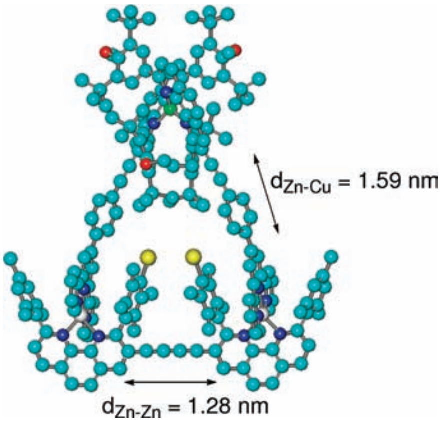

Figure 4. Energy-minimized structure of isosceles triangle $\mathbf{T_0}$ (hydrogen atoms are removed for clarity). Counteranions are not included because ^{19}F NMR spectra indicated them to be free (see the Supporting Information).

The direct relationship between the geometry and the redox potential of copper(I) complexes[15] prompted us to investigate the redox behavior of the triangles $\mathbf{T}_n$. Because the bisecting angle between the two phenanthrolines at the copper(I) center is expected to vary with the changing length of the bisphenanthroline $\mathbf{B}_n$, a change in the redox potential was expected. Differential pulse voltammetry of the triangles $\mathbf{T}_n$ reflected this trend. Although the bulky aromatic groups at the PHENLOCK hinge unit prevent pronounced geometric changes, a shift by 14 mV was observed among the triangles $\mathbf{T}_n$ as a function of $n = 0$, 1, and 2 [$E_{1/2}(\mathbf{T_0}) = 0.798$ V_{SCE}; $E_{1/2}(\mathbf{T_1}) = 0.784$ V_{SCE}; $E_{1/2}(\mathbf{T_2}) = 0.784$ V_{SCE}; Supporting Information].

In conclusion, we have fabricated the first supramolecular triangles $\mathbf{T}_n$, which are heterometallic and isosceles, both geometrically and chemically. They contain two different metals, two different ligands, and multiple binding motifs. Despite such complexity, the yield is quantitative. The angular hinge **A** is a key to the successful realization of $\mathbf{T}_n$ because it is able to adapt to the length of the bisphenanthroline $\mathbf{B}_n$, clearly seen from ^{1}H NMR and redox data. Thus, the assemblies are not only a class of challenging nanoarchitectures but also promising test cases for nanomechanical devices,[16] such as adjustable tweezers.[17]

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Supporting Information Available: Experimental procedures and spectroscopic data provided for **A** and $\mathbf{T}_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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