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Stoichiometric Self-Assembly of Isomeric, Shape-Persistent, Supramacromolecular Bowtie and Butterfly Structures

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S Supporting Information

ABSTRACT: Two novel macromolecular constitutional isomers have been self-assembled from previously unreported terpyridine ligands in a three-component system. The terpyridine ligands were synthesized in high yields via a key Suzuki coupling. Restrictions of the possible outcomes for self-assembly ultimately provided optimum conditions for isolation of either a molecular bowtie or its isomeric butterfly motif. These isomers have been characterized by ESI-MS, TWIM-MS, ¹H NMR, and ¹³C NMR. Notably, these structural isomers have remarkably different drift times in ion mobility separation, corresponding to different sizes and shapes at high charge states.

The past 20 years have brought major advances in the field of supramolecular chemistry. Lehn,^{1,2} Stang,³ Fujita,^{4–7} Schmittel,^{8–12} and others have reported numerous examples of novel macromolecules that rely on <ligand–M–ligand> connectivity as a driving force for assembly. While homoleptic self-assembly is typically quite facile,^{13,14} heteroleptic self-assembly is often more difficult.^{11,15–18} Typically, directed and self-assembly techniques are combined^{19–22} in the synthesis of large metallocycles,²³ rectangles,^{24–26} and other polygons.^{15,27–29} These recent developments enhanced the insights into molecular self-assembly of higher ordered superstructures. Of the numerous examples, several have utilized <tpy–M²⁺–tpy> (tpy = terpyridine) connectivity as a means of constructing multicomponent systems.^{29–31}

In particular, we have recently reported the use of <tpy–M²⁺–tpy> connectivity for the facile construction of a hexagonal spoked wheel,³⁰ represented by Figure 1A, which is composed of six individual triangles with shared sides that exhibit isomeric patterns, such as end-to-end triangles (Figure 1B,C), possessing differing orientations about a mutual point. This is an example of discrete control over the supramacromolecular self-assembly of bicyclic, polygonal constitutional isomers; notably, monocyclic stereoisomers, syn/anti-isomers, linkage isomers, and supramolecular isomers along with isomeric nanobaskets have been reported.³² We herein report the synthesis of novel bis- and tetrakis-terpyridine ligands and their use in the construction of isomeric, triad-based, bicyclic architectures.

Recent advances in mass spectrometry (MS) have been key factors in better understanding the principles of supramolecular construction. The use of traveling wave ion mobility (TWIM)-

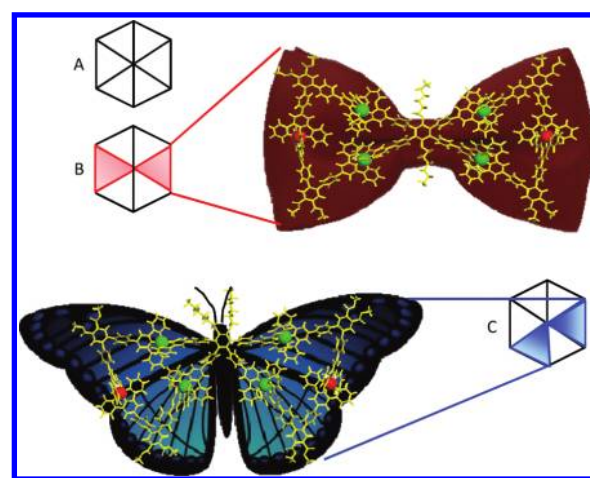


Figure 1. Hexagonal spoked-wheel motif (A) and isomeric triangular polygons (B,C) along with their corresponding terpyridine-based metallocyclic representations (counterions omitted for clarity).

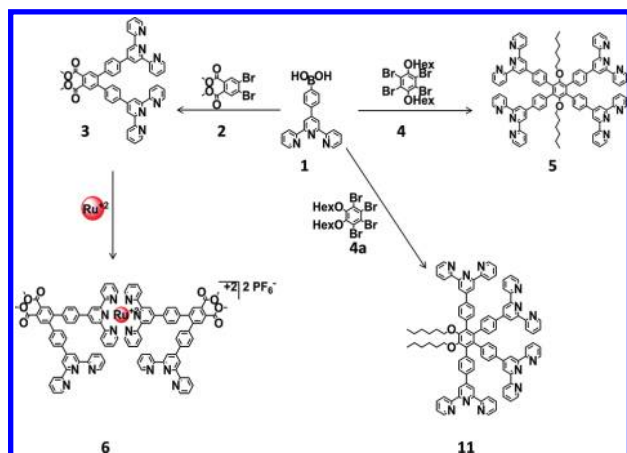
MS coupled with electrospray ionization (ESI)-MS has afforded mass, charge, and size differentiation in the characterization of these species by allowing the observation of the higher charge states without fragmenting the labile metal–ligand connections of the self-assembled product.^{13,30,33}

Prior to this technique, it was often impossible to get acceptable MS data,^{13,34,35} and in cases where there were multiple components, the ¹H NMR spectra would often be extremely complex and inconclusive. Also, if there were undesirable side products resulting from kinetic instability, their structural characterization could be difficult.

The critical bis-terpyridine ligand **3** was successfully synthesized (Scheme 1) by Suzuki cross-coupling of 4,5-dibromo-1,2-bis-carbomethoxybenzene (**2**)³⁶ with excess 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (**1**) in a H₂O:toluene:*t*-BuOH mixture (3:3:1 v/v/v) for 48 h. Column chromatography (Al₂O₃, CHCl₃) followed by recrystallization afforded (51%) bis-terpyridine **3**. Characterization included pertinent ¹H NMR resonances, such as a singlet at 8.71 ppm and a doublet at 8.65 ppm assigned to the 3',5'- and 6,6''-tpyH, respectively; all other resonances were readily assignable. An ESI-MS peak at *m/z* 809.2, consistent with [M+H]⁺, also supported the structural assignment. Ligand **3** maintained the ¹H NMR

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Scheme 1. Synthesis of 3, 5, 6, and 7^a

^aLigands 3, 5, and 7 were synthesized from 2, 4, or 4a, respectively, with 1 and isolated in good yields.

marker resonance (CO_2CH_3) at 4.0 ppm, allowing for structural comparisons.

Alkoxy-modified, tetrakis-terpyridine 5 was prepared (84%, Scheme 1) from 1 and 4 using a protocol similar to that used for 3. The ^1H NMR spectrum of 5 (Figure 3) exhibited a single set of resonances for the terpyridine moieties that was nearly identical to that of 3, as well as the expected symmetrical absorptions for the aryl core; an ESI-MS peak for $[\text{M}+\text{H}]^+$ at m/z 1508.0 corroborated the assignment. Initial attempts to obtain the desired bowtie 9 using 3, 5, and Cd^{2+} (or Zn^{2+}), in a 4:1:6 stoichiometry, respectively, gave a triangle 8 as the major component along with bowtie 9, as shown by both ESI-MS (Figure 2) and NMR analyses. Notably, prior attempts using

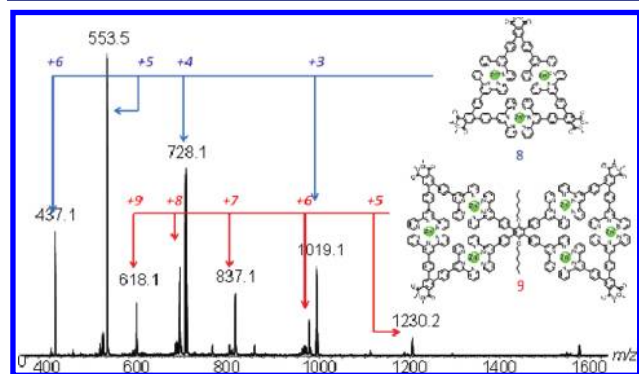


Figure 2. One-dimensional ESI-MS of the mixture of 8 and 9, with pertinent charge states marked. Counterions (BF_4^-) are omitted from the structures for clarity.

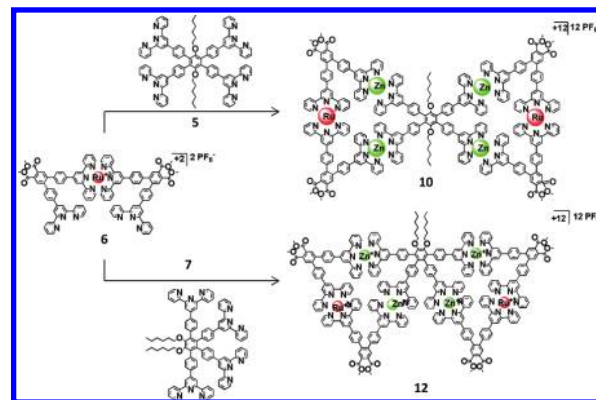
this procedure and the methoxy-modified analogue of bis-ligand 3 (3-OMe, SI-p16) led to more favorable yet similar undesirable mixtures.

Modifications aimed at eliminating the formation of trimer 8 focused on restricting the degrees of freedom. Thus, a Ru^{II} dimer was targeted to instill a nonreversible complex between the two outer 60° ligands. Dimer 6 was prepared (40%) from the stoichiometric reaction of bis-ligand 3 with $\text{RuCl}_2(\text{DMSO})_4$ ³⁷ in a refluxing CHCl_3 :MeOH mixture (1:1 v/v), followed by column chromatography (Al_2O_3 , $\text{CHCl}_3 \rightarrow \text{MeCN}:\text{H}_2\text{O}:\text{sat. KNO}_3(\text{aq})$ 25:1:1 v/v/v); small oligomers were also isolated (22%), based on ^1H NMR. Dimer 6 was

characterized by the expected two sets of resonances (^1H NMR) with an integration ratio of 1:1 for the complexed and metal-free terpyridine ligands (Figure S1). The MALDI-MS was consistent with dimer formation, exhibiting a peak at m/z 1843.91.

Reaction of the bis-terpyridine dimer 6 with the alkyl-modified tetrakis-terpyridine 5 and $\text{Zn}(\text{BF}_4)_2$ in a 2:1:4 stoichiometric ratio afforded the heterometal bowtie polygon 10 (Scheme 2), with no observable tetrameric starting material.

Scheme 2. Synthesis of the Zn^{II} Analogues of the Bis-triangles 10 and 12 with 2 equiv of 6 (25 $^\circ\text{C}$, 1 h)



The ^1H NMR spectrum of 10 exhibited peaks in the expected 6:1 ratio corresponding to the $-\text{CO}_2\text{CH}_3$: $-\text{OCH}_2\text{R}$ moieties (see Supporting Information). Although this creates the potential for self-assembly of 6 and the *meta*-substituted terpyridines of 5, the strain of this type of bonding would be enthalpically disfavored over the structure depicted in Scheme 2.

COSY analysis simplified assignment of all resonances in the aromatic region of the ^1H NMR. Notable attributes of the ^1H NMR spectrum of 10 (Figure 3) include three discernible sets of 3',5' resonances, two of which partially overlap but exhibit an ideal 1:2 integration, and the 3,3'' and 6,6'' resonances, which displayed the desired downfield and upfield trends, respectively. Results from ESI-MS and TWIM-MS (Figures 4 and S2) showed that bowtie 10 with either Zn^{II} or Cd^{II} was the predominant component. Based on the sharp drift time

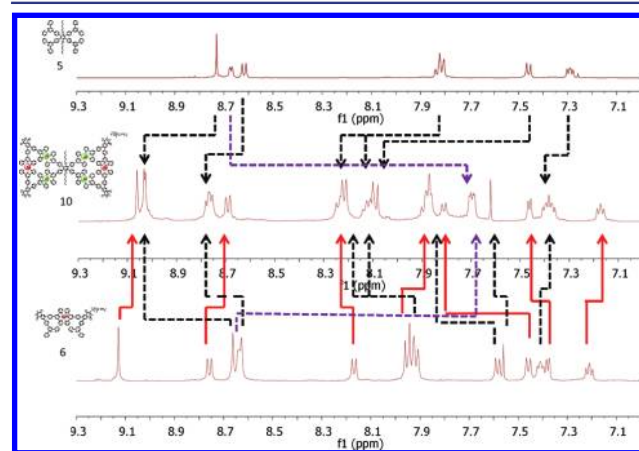


Figure 3. ^1H NMR overlay of starting materials 5 (top) and 6 (bottom) with the Zn bowtie 10 in the center. Arrows depict assigned resonance shifts that occur upon complex formation.

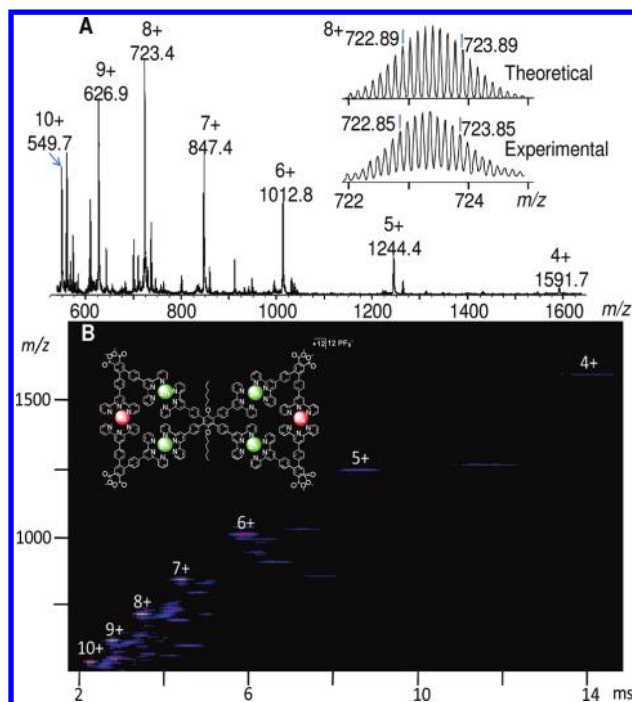


Figure 4. (A) ESI-MS and (B) 2D ESI-TWIM-MS plot (mass-to-charge ratio vs drift time) of **10**. The charge states of intact assemblies are marked.

distribution of the different charge states, no other component was detected in TWIM-MS, reflecting the highly rigid shape-persistence of this bowtie-type architecture. Additionally, Zn^{II} and Cd^{II} give complexes of the same size, as the corresponding drift times of each charge state are nearly identical (Table S3).

In view of this result, can one discern the difference between two isomeric structures, for example, via differences in MS drift times or collision cross sections? This was tested by preparing the related butterfly motif **12** by the self-assembly of ligands **7** [accessed by Suzuki coupling of 1,2,3,4-tetrabromo-5,6-bis-hexoxybenzene (**4a**, Scheme 1) to the terpyridine boronic acid **1**] and **6** (Scheme 2). The tetrakis-terpyridyl product revealed two distinct sets of resonances that are easily differentiable (see spectra in the Supporting Information). Based on modeling of isomers **10** and **12**, there is a difference in size or theoretical cross section value for the two species; thus, one would expect a difference between these isomers in the TWIM-MS.

Butterfly **12** was readily assembled, resulting in a 1D ESI-MS (Figure S5) nearly identical to that of **10** (Figure S4); however, the TWIM-MS drift times were different at low charge states, e.g., 4+ to 6+. Notably, the bowtie complex **10** has a significantly larger collision cross section than that of its butterfly-shaped isomer **12** (Figure 5). As the charge increases, both isomers have very similar drift times or cross sections (Table S3). Thus, the charge distribution affects the sizes of these two complexes at low charge states, but once the 7+ charge state is reached, there are marginal differences between the two.

In summary, two novel supramolecular isomers have been isolated via a three-component self-assembly. These bowtie and butterfly-type structures were predesigned to utilize $\langle \text{tpy}-\text{M}^{2+}-\text{tpy} \rangle$ connectivity, where M^{2+} is either Cd^{2+} or Zn^{2+} . Initial attempts provided a mixture of a small triangle as well as the desired structure. Restriction of the components' degrees of freedom by preparation of a Ru^{2+} dimer led to isolation of pure

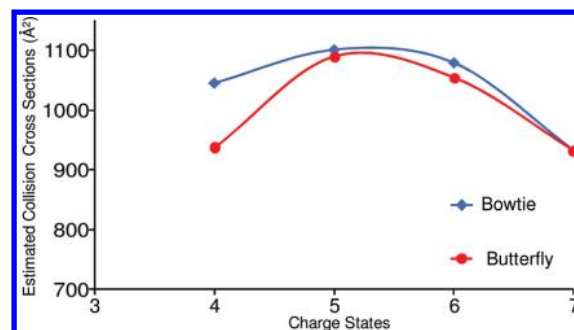


Figure 5. Comparison of the estimated collision cross sections of bowtie **10** and butterfly **12** at different charge states, i.e., 4+ to 7+.

bis-triangular supramolecular structures that were elucidated by ^1H and COSY NMR, as well as ESI-TWIM-MS. While the one-dimensional ESI-MS data were identical for the isomers, the TWIM-MS data revealed notable differences regarding detailed size and structure information. Comparison of the drift times of the two isomers showed a significant difference in the low charge states for the two isomers, whereas the drift times of the higher charge states remained nearly identical. Further utilitarian studies of these isomers and related materials are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

All pertinent spectral data and complete experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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