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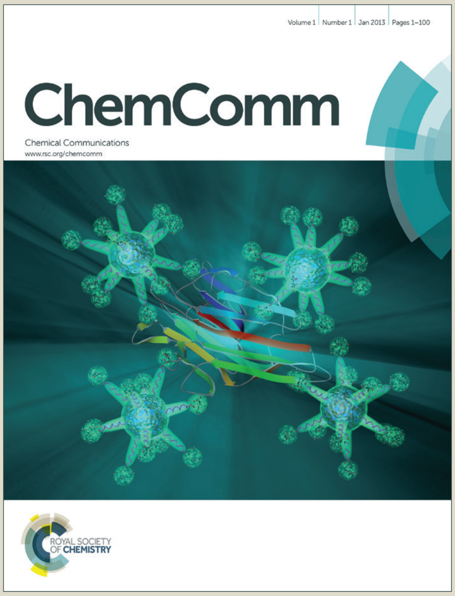

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ARTICLE TYPE

Multicomponent Reassembly of Terpyridine-based Materials: Quantitative Metallomacrocyclic Rearrangement

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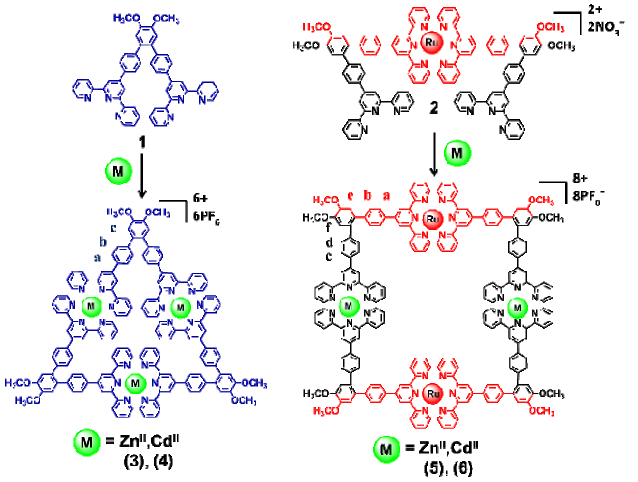
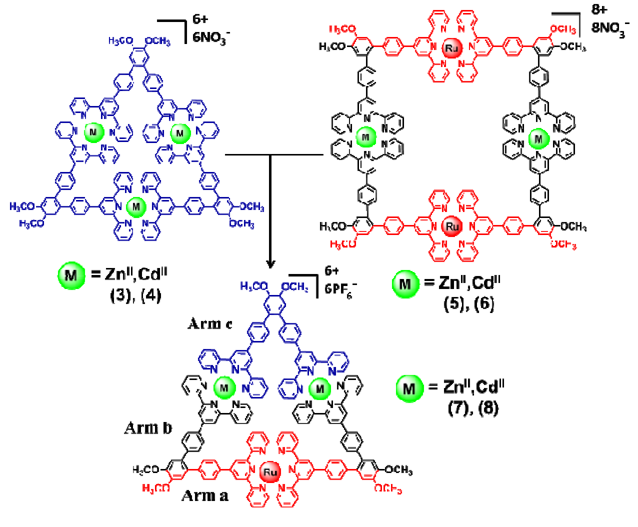
Mixing of metallocyclic trimers and tetramers in an exact 1:1.5 stoichiometry provided new supramolecular triangles in quantitative yields. Characterization of the new hetero-nuclear metallomacrocycles was achieved by ^{1}H, 2D-COSY, 2D-NOESY, and ^{13}C NMR spectroscopy, along with ESI and TWIM mass spectrometry. Gradient tandem MS (gMS^2) provided insight into the stabilities of the binuclear structures.



Scheme 1. Synthesis of triangle **3** and **4**[32]and tetramer **5** and **6**[33].

Inspiration from supramolecular biological assemblies[1-3] has paved the way for many diverse and intricate structures. As well, pioneering studies by Lehn[4] and later by Stoddart,[5] Fujita,[6] Stang,[7] Meijer,[8] Schmittel,[9] Newkome[10] and others[11-17] have successfully employed non-covalent interactions to prepare well-defined, complex architectures. Among these binding interactions, coordination-driven assembly has ascended in importance due to the availability of a wide variety of ligands and metal ions.[18,19] More specifically, 2,2':6',2"-terpyridine-based building blocks have drawn extensive attention due to their ability to form stable tpy-M^{II}-tpy complexes, while allowing the incorporation of utilitarian structural features.[20] The majority of metallosupramolecular constructs utilize symmetric monomers involving homoleptic assemblies;[21] however, the scope of heteroleptic assemblies involving two or more components has been limited due to their inherent tendency to produce competitive products resulting from self-sorting.[22,23] Growing interest to incorporate greater structural complexity into molecular motifs *via* heteroleptic assemblies has been challenging.[24] Schmittel *et al.*[25] have reported an eloquent catalytic "fusion-like assembly," reminiscent of "gene shuffling," to obtain *tris*heterometallic scalene triangles by combining rectangular and equilateral motifs. Similarly, Stang and co-workers[26] have described the stoichiometric conversion of two homoleptic architectures into a heteroleptic structure. Recently, we reported the assembly of a variety of structures, such as a binuclear hexamer,[27] isomeric molecular bow-tie and butterfly,[28] hexagonal spoked-wheel,[29] and a molecular rhombus[30] using heteroleptic protocols.

Herein, we report the synthesis of novel terpyridine-based bimetallic triangles *via* the metallomacrocyclic rearrangement of a metallotriangle with a metallosquare; ramifications include the utility of shape-specific, supramolecular species as multicomponent donors.



Scheme 2. Quantitative rearrangement of triangle **3** and **4** with tetramer **5** and **6**, respectively, to generate bimetallic triangles **7** and **8**. Arm **a**, **b**, and **c** are marked to augment the ^{1}H NMR assignments in the text.

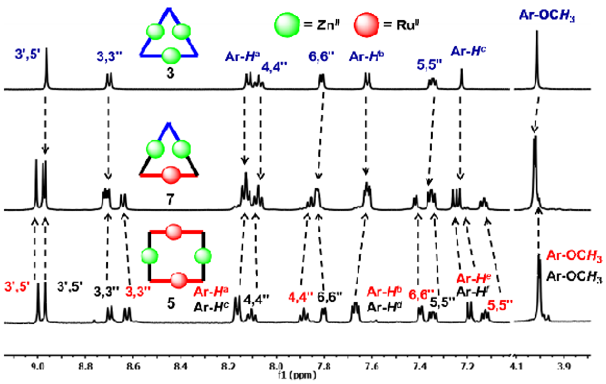


Figure 1. Stacked ^{1}H NMR spectra (500 MHz) of triangle **3** (top), tetramer **5** (bottom), and triangle **7** in CD_3CN (center).

Initially, the known *bis*terpyridine[31] **1** (prepared by a Suzuki cross-coupling from 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine and 4,5-dibromo-1,2-dimethoxybenzene[27]) was used to prepare dimer **2**.[33] The homoleptic triangles **3** and **4** were obtained in quantitative yield by reacting ligand **1** with either Zn(II) or Cd(II), respectively.[32] Tetrameric constructs **5** and **6** were synthesized from dimer **2** by reacting it with Zn(II) or Cd(II) respectively, in a good yields.[33] Triangles **3** and **4** and tetramers **5** and **6** were unambiguously characterized by NMR and ESI-MS spectrometry.

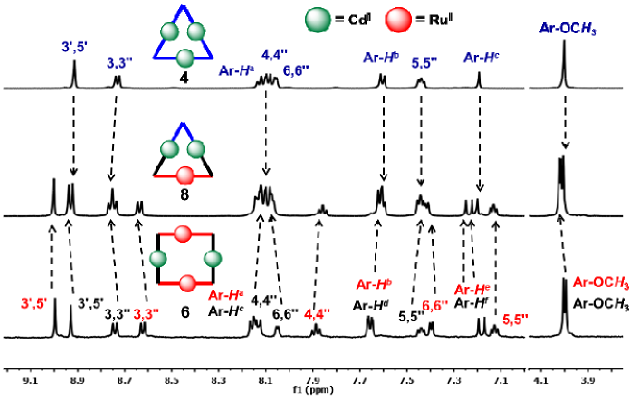


Figure 2. Stacked ^{1}H NMR spectra (500 MHz) of reagents **4** (top), **6** (bottom) as well as triangle **8** in CD_3CN (center)

To Zn-triangle **3** in MeOH, a solution of Ru-Zn-tetramer **5** in MeOH was added in a precise 1:1.5 molar ratio. The reaction mixture was stirred at 25 °C for 30 min., then a saturated solution of NH_4PF_6 in MeOH was added to exchange the counterions. The PF_6 complex was repeatedly washed with MeOH to remove excess NH_4PF_6 affording (98%) pure bimetallic triangle **7**, as an orange solid; triangle **8** was synthesized (99%) *via* an identical procedure.

The new materials **7** and **8** were unequivocally characterized by ^{1}H, COSY, NOESY, and ^{13}C NMR spectroscopies along with ESI and TWIM-MS. Thus, the well-resolved ^{1}H NMR spectra of **7** (Figure 1) and **8** (Figure 2) indicated the presence of a single discrete composition; notably, distinguishing features included signals from three different 3',5'-tpy protons (9.00, 8.97, and 8.96 ppm for **7** and 9.00, 8.94, and 8.92 ppm for **8**) corresponding to arms **a**, **b**, and **c** (Scheme 2) with an 1:1:1 integration ratio, which is in agreement with the proposed structures. The 3,3'' and 6,6'' protons in both heterometallic triangles **7** and **8** showed the expected upfield and downfield shifts derived from complexation. The methoxy markers exhibited peaks at 4.03, 4.02, 4.01 ppm and 4.02, 4.01, 4.00 ppm for **7** and **8**, respectively, each with a precise 1:1:1 integration ratio, providing additional support for both macrocycles. All other terpyridine and aromatic proton assignments were verified with 2D-COSY and NOESY experiments.

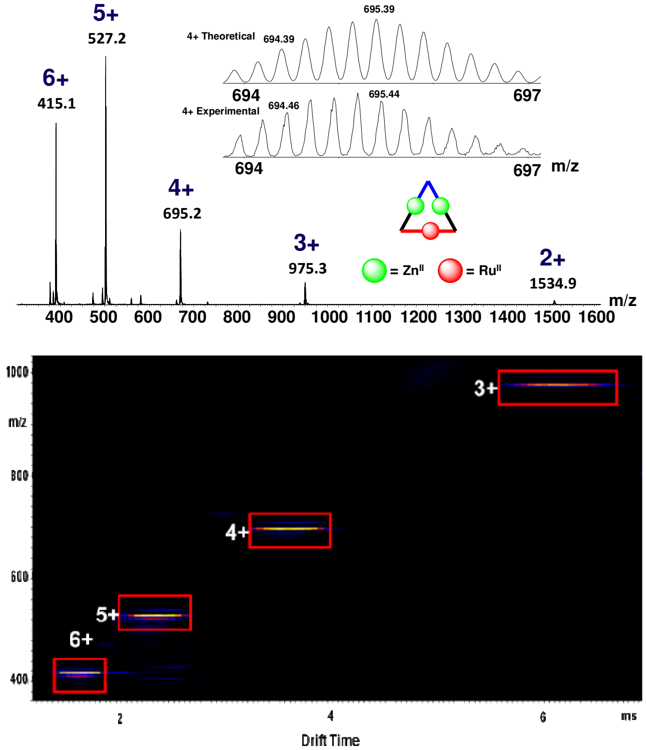


Figure 3. (A)The ESI-MS spectrum with calculated and experimental isotope patterns for the 4+ species and (B) 2D ESI-TWIM-MS plot (mass-to-charge ratio *vs* drift time) for **7**. The charge states of intact assemblies are marked.

Fused metallocycles **7** and **8** were further characterized by ESI-MS coupled with TWIM-MS. In the ESI-MS spectrum of **7** (Figure 3A), a series of dominant peaks was observed at *m/z* 415.1, 527.2, 695.2, 975.3, and 1534.9 corresponding to charge states 6+ to 2+ generated by the loss of PF_6^- anions. In comparison, the ESI-MS spectrum of **8** (Figure 4A) also exhibited a similar series of peaks at *m/z* 430.1, 546.8, 718.2, 1006.9, and 1582.4. The TWIM-MS data for both **7** and **8** (Figures 3B and 4B, respectively) show a set of single and narrow bands for charge states 6+ to 3+; this is in agreement with the presence of a single discrete product.

Alternatively, triangle **7** and **8** could be directly constructed from **1** and **2**. For this, to an exact 1:1 mixture of ligand **1** and dimer **2** in $CHCl_3$, a MeOH solution of 2 equivalents of either $Zn(NO_3)_2{\cdot}6H_2O$ or $Cd(NO_3)_2{\cdot}4H_2O$ was added followed by stirring for 30 min. at 25 °C. The counterions were changed to PF_6^- and both the bimetallic triangles **7** and **8** were recovered in quantitative yield. All spectral data of **7** and **8**, synthesized by either method, were identical.

In addition, gradient tandem mass spectrometry (gMS^2)

experiments were performed on both **7** and **8** to evaluate the stability of these bimetallic metallocycles and to gain insight into their use as reagents to generate more complicated structures. The 5+ ion of **7** (SI Figure S21) at *m/z* 527.2 was exposed to collisionally activated dissociation, revealing stability up to 20 eV; the 5+ charge state almost dissipated at 35 eV, corresponding to a center-of-mass (COM) collision energy of 1.74 eV. Using similar experimental conditions, the gMS^2 spectra for **8** were obtained (SI Figure S22). The experiment revealed that triangle **8** is slightly less stable when compared with **7**. The 5+ charge (at *m/z* 546.8) state of complex **8** completely disappeared at 33 eV, corresponding to a COM collision energy of 1.62 eV. In comparison, COM collision energy for triangle **3** and **4** are 1.81 eV and 1.75 eV respectively[32] and that for tetramer **5** and **6** are 1.64 and 1.53 eV, respectively.[33]

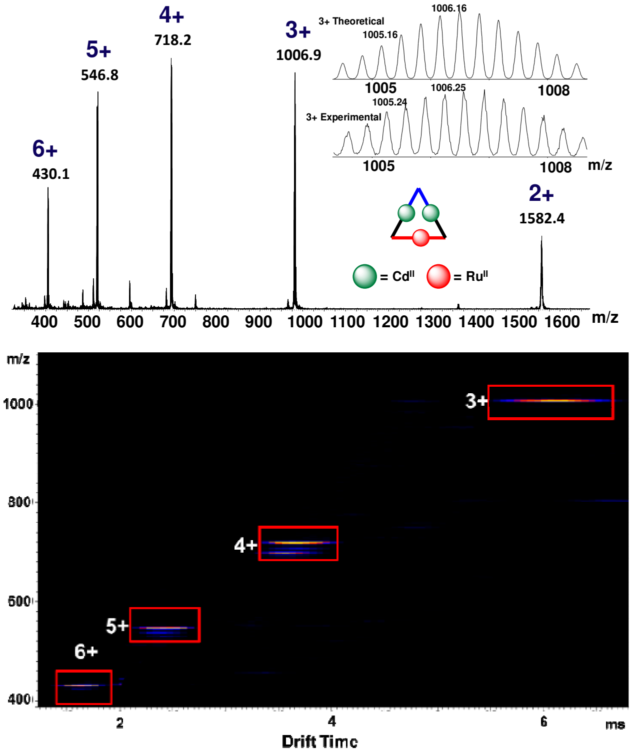


Figure 4. (A) ESI-MS spectrum of **8** with calculated and experimental isotope patterns for the 3+ species and (B) 2D ESI-TWIM-MS plot (mass-to-charge ratio *vs* drift time) of **8**. The charge states of intact assemblies are indicated.

^{1}H NMR titration experiments were performed to follow product formation. Thus, tetramers **5** and **6** were added in increasingly greater stoichiometric ratios to triangles **3** and **4**, respectively. The ^{1}H NMR spectra (SI Figures S15 and S16) exhibit the formation of triangles **7** and **8** by the sequential appearance of product peaks; non-cyclic intermediates were not observed. The dynamic equilibrium between ligand **1** and dimer **2** in presence of a kinetically labile metal ion, such as Zn(II) or Cd(II), quantitatively produced binuclear **5** and **6**, which can be attributed to entropy maximization.[34] Due to the low complexation energy of both Zn(II)-tpy and Cd(II)-tpy,[35] dynamic equilibria involving these two metal ions tend to produce the maximum number of molecules possible to maximize entropy, which in turn compensates for the low complexation energy. As the "*self-sorting*" of ligand **1** and dimer **2** produces less species compared to their heteroleptic assembly producing **5** or **6**, the dynamic equilibrium prefers the latter.

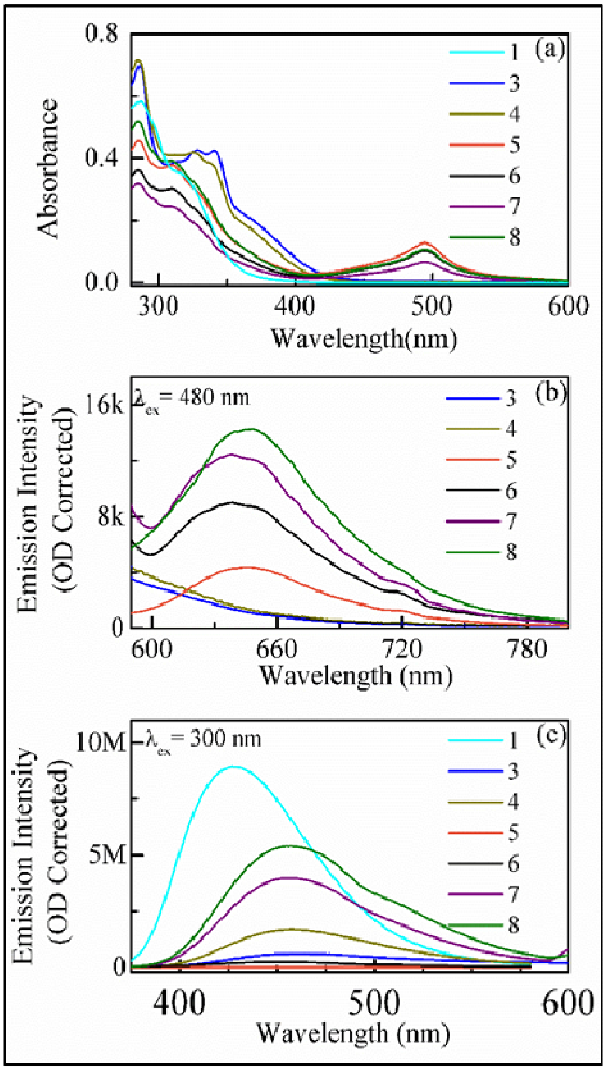


Figure 5. (a) Normalized UV-Visible spectra of **1** and **3-8**. (b) Corrected emission spectra of **3** - **8** by at the excitation wavelength λ_{ex}=480 nm. (c) Corrected emission spectra of **1** and **3-8** by at the excitation wavelength λ_{ex} = 300 nm.

The photophysical properties of **1** and **3** - **8** have been studied using steady state absorption spectroscopy and fluorescence spectroscopy. Their absorption spectra are presented in Figure 5(a). Ligand **1** exhibits typical ligand to ligand (LL) π-π* charge transfer (CT) bands at 285 and 330 nm localized on the terpyridine-phenyl subunit. Complexation with Ru(II) results in a metal-ligand charge transfer (MLCT) band at 483 nm due to CT active Ru(II) center; however, a MLCT band is not observed in the tpy-Cd(II)-tpy and tpy-Zn(II)-tpy complexes. All photoluminescence spectra are corrected for fluctuation in absorbance. The emission intensities of **7** and **8** are higher than the intensities of bimetallic tetramers **5** and **6** at both excitation wavelengths 480 and 300 nm (Figure 5(b, c). All Cd(II)-complexes showed higher emission intensities compared to their

Zn(II) analogues probably due to the stronger quenching effect of Zn(II).[36,37] Ligand centered π-π* CT bands of **1** experienced a red shift (Figure **5c**) upon complexation presumably due to an increase in the non-radiative decay process.

Conclusions

Two novel terpyridine-based heterometallic triangles were constructed in quantitative yield by the facile interconversion of triangular and tetrameric metallomacrocyclic species. Both constructs **7** and **8** were unequivocally characterized using ^{1}H, COSY, NOESY and ^{13}C NMR spectroscopy, as well as ESI and TWIM-MS. The preparation of these binuclear, precise molecular triangles in high yield supports their use as multicomponent reagents in the construction of complex supramacromolecular materials.

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ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data including COSY, NOESY and ^{13}C NMR, ESI-MS, tandem mass spectrum, UV/Vis absorption spectrum. This material is available free-of-charge *via* the Internet at http://rsc.org.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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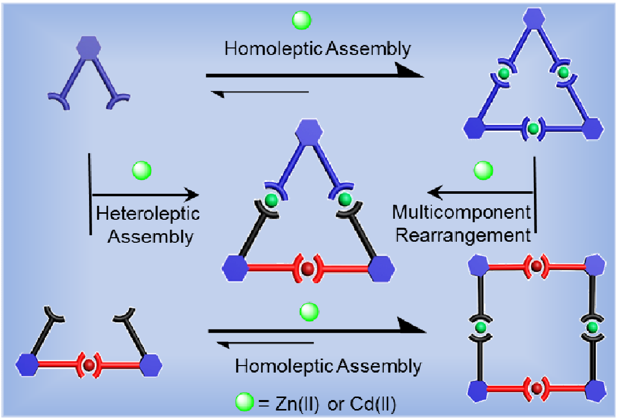

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