

Construction of a Highly Symmetric Nanosphere via a One-Pot Reaction of a Tristerpyridine Ligand with Ru(II)

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Supporting Information

ABSTRACT: A three-dimensional, highly symmetric, terpyridine-based, spherical complex was synthesized via the coordination of four novel, trisdentate ligands and six Ru²⁺ ions, and it exhibits excellent stability over a wide range of pH values (1–14). Structural confirmation was obtained by NMR and ESI-TWIM-MS.

Coordination-driven supramolecular chemistry has experienced an extraordinary rise in interest and development.¹ Numerous 3D nanoscopic architectures built by metal–ligand interactions have been created using shape-enforcing organic building blocks, based on diverse coordination moieties, such as pyridine,² carboxylate,³ catechol,⁴ acetyl-acetone,⁵ and others.⁶ To date, few terpyridinyl-based ligands have been used to construct 3D nanoscopic structures, due in-part to limited access to complex terpyridinyl building blocks and to unexpected coordination possibilities.^{7,8} However, predicated on the rich chemistry of the terpyridine moiety, its potential for complex formation, and the resulting electronic properties, the attraction for its use to construct new 3D nanoarchitectures is compelling. Toward this end, the easily prepared synthon terpyridinyl(phenyl)boronic acid⁹ has paved the way toward the construction of novel terpyridine-based building blocks and new supramolecules.

Another criterion to be considered for ligand-based, nanostructure construction is the stability of the metal complex;¹⁰ for example, kinetically dominated complexation increases in the order Cd²⁺ < Zn²⁺ < Fe²⁺ < Ru²⁺ ≤ Os²⁺. Thus, thermodynamic control over the self-assembly process in these cases is essentially lost when metals, such as Ru and Os, are employed, since once the complex is formed, it is irreversible. Although utilizing the less labile metal ions for construction involving multiple ligand–metal–ligand connectivity can be challenging, advantages include the potential to easily isolate and purify the reaction products. A few methods that take advantage of thermodynamic equilibria have been reported, such as utilizing photochemistry,^{11a} ionic activity,^{11b} or solvent polarity.^{11c} Divergent and convergent stepwise assemblies,¹² in many cases, are the logical choices when multiple Ru²⁺ complexes are required to form the desired product.

Herein, we report the first example of a single-step, kinetically controlled assembly of a nanosized, highly symmetric, supramolecular sphere **4** in moderate to good yields (i.e., 35%) through the combination of four trisdentate terpyridinyl building blocks with six Ru²⁺ ions; structural confirmation was accomplished using 1D and 2D NMR and ESI-TWIM-MS methods. We attribute the successful generation of these nanospheres with six kinetically driven, bis-ligand-Ru connections, in large part, to the precisely designed, perfect fit of the quasi-shape-persistent ligand **3** in contrast to entropically favored formation of a finite symmetrical species relative to that of polymeric structures under thermodynamic control.¹³ In comparison to the cage-like, metal–organic framework supramolecules (MOFs),^{1,14} which show either alkali or acid resistance, the spherical hexaRu complex **4** exhibits excellent stability in the presence of both strong acid as well as strong base, such as concentrated nitric acid and sodium hydroxide (1 M), and at high temperatures [based on TGA data showing that degradation begins at 370 °C (Figure S15)]; the ¹H NMR spectrum remained essentially constant under all conditions (Figure S10) suggesting potential applications in supramolecular catalysis.¹⁵

Construction of the highly symmetric 3D structure **4** (Scheme 1) was accomplished using the key intermediate 3-(2,2':6',2''-terpyridinyl)phenylboronic acid^{8b} (**2**) that was prepared using the commercially available 3-formylphenylboronic acid. The 1,3-substitution on the phenyl spacer instilled the critical angle necessary for the building block to adopt the observed cap-like conformation.¹⁶ A triple Suzuki-coupling reaction using tris(4-bromophenyl)benzene (**1**) and ligand **2** subsequently gave (70%) the desired trisdentate ligand **3**. The ¹H NMR spectrum of the trisligand **3** (Figure 1) exhibited one set of expected signals attributed to the terpyridinyl moieties and a single set of peaks assigned to the aryl groups suggesting free rotation throughout the three terpyridinyl arms.

Treatment of the ligand **3** with Ru(DMSO)₄Cl₂¹⁷ (2:3 ratio) in a refluxing MeOH and CHCl₃ (1:2 v/v) for 24 h gave a deep red translucent solution. After evaporating the solvent, the residue was purified by flash column chromatography (silica) eluting with a mixture of MeCN, saturated aqueous KNO₃, and

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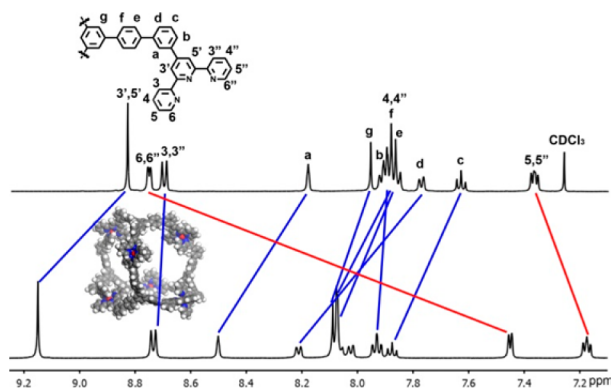
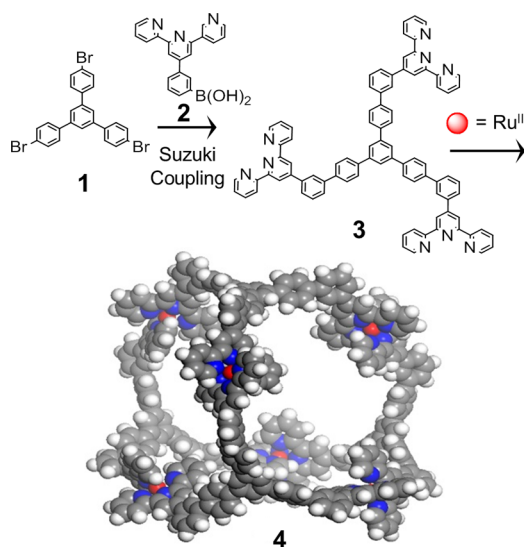
Scheme 1. Synthesis of the Ru²⁺-Based, Metallo-Nanosphere Using Ru(DMSO)₄Cl₂ (counterions omitted)


Figure 1. ¹H NMR spectra (500 MHz, 300 K) of ligand **3** in CDCl₃ and complex **4** in CD₃OD and CD₃CN (1:3 v/v).

water (20:1:1 v/v). Subsequent washing with H₂O removed the excess nitrate salt to afford (35%) the desired complex **4** with nitrate counterions. Additional fractions isolated from the column were analyzed and determined to be intermediate nanosphere fragments.

The 1D ¹H NMR spectrum of complex **4**, using a mixture of CD₃OD and CD₃CN (1:1) at 25 °C, exhibited one set of sharp and well-resolved peaks (Figure 1) indicative of the formation of a single and highly symmetrical species, in which all identical nuclei are chemically and magnetically equivalent. COSY and 2D NOESY NMR experiments were used to aid in the assignment of the different patterns. Both the characteristic downfield shift of the singlet assigned to the tpyH^{3',5'}s at 9.15 ppm and the upfield shift ($\Delta\delta = 1.3$ ppm) of the tpyH^{6,6''} doublet are indicative of complex formation. Notably, the signals assigned to the tpyH^{5,5''}s, upon complexation, exhibit a slight upfield shift ($\Delta\delta = 0.2$ ppm) in contrast to the usually observed small downfield shift.¹² This suggests a slow rotation of the individual complexes within the nanosphere's framework.¹⁸

The ESI-MS spectrum of complex **4** (Figure 2a) with nitrate anions further supports the structure of the nanosphere by revealing a series of dominant peaks at *m/z* 460.09, 507.6, 564.5, 634.0, 720.9, 832.9, 982.2, and 1191.2 corresponding to

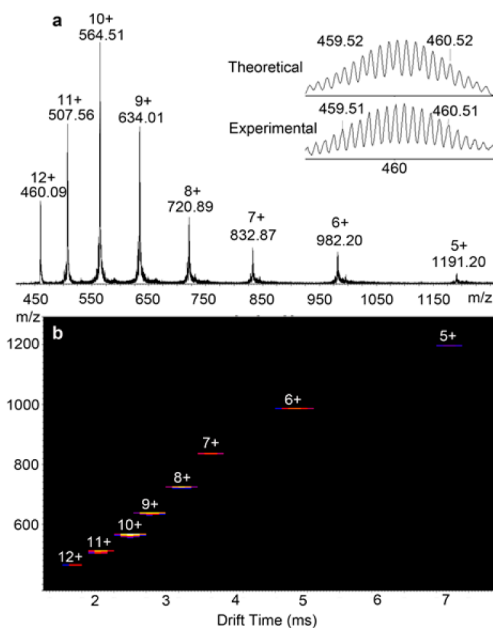


Figure 2. (a) ESI-MS spectrum of **4** with the isotope cluster of the 12+ charge state shown in the inset. (b) ESI-TWIM-MS plot of **4** (*m/z* vs drift time) with the charge states of intact assemblies marked.

the charge states from 12+ to 5+, respectively. The experimental *m/z* values and isotope patterns for each charge state are consistent with the respective calculated values. Additional evidence (Figure 2b) for the structure of **4** was provided by ESI-TWIM-MS experiments (ESI-MS coupled with traveling-wave ion mobility spectrometry, a variant of ion mobility spectrometry).¹⁹ TWIM-MS resembles a chromatography method, separating ions by their charge and shape/size in the TWIM region and by *m/z* in the mass analyzer following this region. Charge states of 12+ to 5+ derived from **4** all show single and narrow signals on the 2D TWIM-MS plot that when extracted, give single peaks with narrow drift time distributions, clearly indicating a single architecture; this is consistent with the NMR results.

The stability of the complex **4** was examined with gradient tandem MS (gMS²). For this experiment, 5+ charge ions (*m/z* 1191.2) were isolated and subjected to collisionally activated dissociation (CAD) prior to ion mobility separation at collision energies ranging from 10 to 55 eV. The nanosphere exhibits good stability, in agreement with other <tpy-Ru²⁺-tpy> complexes.^{12c} Only when the collision energy reached 52 eV, the 5+ complex ion (*m/z* 1191.2) completely disappeared, yielding several fragments (see Figure S11), among them a sizable fragment at *m/z* 1101.4 resulting from the loss of two Ru(NO₃)₂ units.

The geometry and energy-minimized image of complex **4** revealed a highly symmetric and shape-persistent spherical structure. Four tridentate ligands adopt a meso conformation to coordinate with six Ru²⁺ ions, leading to the rigid sphere-shaped structure. The centers of four tridentate ligands form a tetrahedron structure and six Ru²⁺ ions make up a regular octahedron conformation with *T_d* symmetry. The longest distance between two Ru²⁺ is 3.2 nm; with an average distance across the interior of ~20 Å; the inner void volume is ~4000 Å³ suggesting numerous host-guest applications. Further evidence for the nanosphere structure was provided by the collision

cross-section (CCS) determined from the drift times measured in the TWIM-MS experiments.

For the 10+, 9+, and 8+ charge states of **4**, the CCSs are 1014.1, 983.4, and 969.2 Å², respectively. The slight CCS differences between these three charge states (which carry 2, 3, and 4 NO₃⁻ counterions, respectively) indicate that the structure of **4** has a rigid and shape-persistent architecture. The average experimental CCS of all charge states examined (956.0 Å², see Table S1) agrees well with the theoretically predicted CCS for the counterion-free complex (947.6 Å²), which was calculated from the corresponding energy-minimized structure using the trajectory method⁵⁰ that rigorously considers the collision process between ions and the buffer gas in the ion mobility region.

Transmission electron microscopy (TEM) experiments facilitated visualization of sphere-like **4**, revealing directly both the size and shape of individual molecules upon deposition of a dilute (~10⁻⁷ M) MeCN solution of complex **4** with PF₆⁻ counterions on carbon-coated grids (Cu, 400 mesh). The outline of single molecules located on the film with edges and corners can be observed. The average distance (~4.1 nm) between the two edges perfectly fits the size that was obtained from the optimized molecular model (Figure 3 and Figure S16).

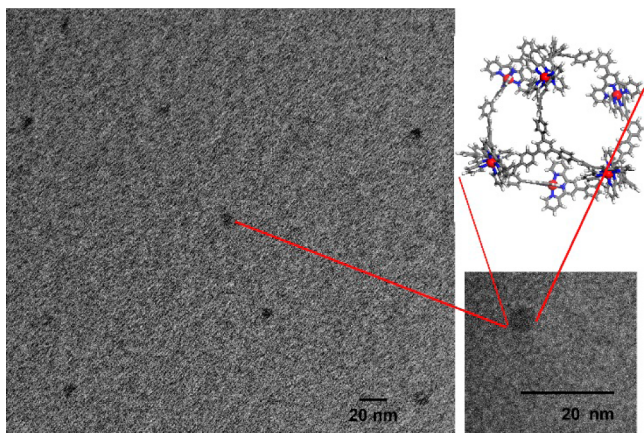


Figure 3. TEM images of complex **4** obtained on a carbon-coated Cu grid and a representative, computer-generated, energy-minimized structure of nanosphere **4**.

In summary, we have designed and synthesized the first terpyridine-based, spherical supramolecule through the combination of four novel tridentate terpyridinyl ligands with six Ru²⁺ ions in a one-step reaction. Unequivocal characterization was accomplished by 1D and 2D NMR experiments, ESI-MS, gMS², and ESI-TWIM-MS analyses, along with molecular modeling. The complex shows good stability under thermal, acidic, or basic conditions. Further investigations concerning host–guest applications, supramolecular catalysis, and aggregation are ongoing.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures and characterization data including COSY and NOESY NMR, ESI-MS, tandem mass spectrum, UV–vis absorption spectrum and TGA data. 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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