

Ruthenium–Cobalt Bimetallic Supramolecular Cages via a Less Symmetric Tetrapyridyl Metalloligand and the Effect of Spacer Units

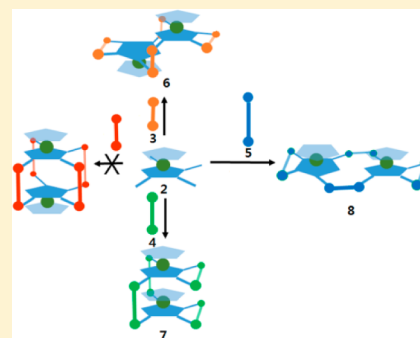
Ji Yeon Ryu,[†] Yu Jin Park,[†] Hyoung-Ryun Park,[†] Manik Lal Saha,[§] Peter J. Stang,^{*,§} and Junseong Lee^{*,†}

[†]Department of Chemistry, Chonnam National University, Gwangju 500-757, Republic of Korea

[§]Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, United States

S Supporting Information

ABSTRACT: The self-assembly of C_3 -symmetric tetrapyridyl cobalt–metalloligand **2** with three half-sandwich diruthenium acceptors, **3–5**, led to the formation of A_4D_2 (A = acceptor, D = donor) metallacages **6–8**, as shown by ESI mass spectrometry, NMR spectroscopy, and X-ray crystallography. The solid-state structures of **6–8** revealed that the length of the acceptor unit greatly influences the molecular packing of these metallacages. Hence, in the solid state, **6–8** can be considered to have waterwheel-shaped, tweezer-shaped, and butterfly-like architectures, respectively.

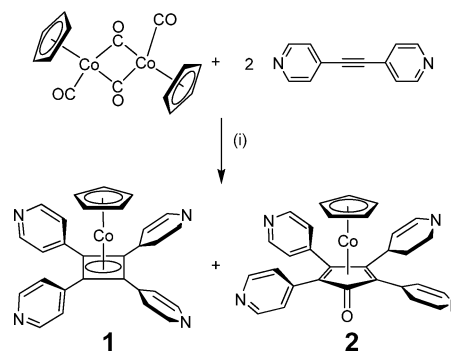


INTRODUCTION

Over the past two decades, coordination-driven self-assembly has been used as an efficient way to construct highly symmetric supramolecular architectures with predetermined shapes and sizes.¹ Consequently, a large number of aesthetically appealing two-dimensional (2D) polygons and three-dimensional (3D) polyhedra with tailor-made properties, such as molecular recognition, intricate host–guest chemistry, modulation of the chemical reactivity of guest molecules, supramolecular catalysis, etc., have been built via the self-assembly of transition-metal-based acceptors and rigid nitrogen/carboxylate donor precursors.^{2,3} In addition to the various organic donors that have been investigated because of their facile syntheses, there has been a growing interest in studying *metalloligand*-based *heterometallic* self-assembled systems as well. Because of the introduction of different metal ions into the assembly, the latter display distinct photophysical, electrochemical, and magnetic properties, which further expand their potential applications as sensors and in material science.^{4–6}

To date, the majority of heterobimetallic complexes have been prepared via the “complex-as-a-ligand” strategy,⁴ in which a kinetically inert metal complex with free binding sites, i.e., metalloligand, is first formed and then mixed with a second metal species to generate larger metallosupramolecular complexes. This technique has proven useful in the creation of many 2D heterometallic assemblies: A_2D_2 rhomboids, A_3D_3 pentagons, and A_3D_3 hexagons (A = acceptor, D = donor) have been successfully constructed via the self-assembly of metal–carbonyl dipyridine ligands and Pt(II)-based acceptors.⁵ However, although there are several reports on the heterometallic assembly,⁷ 3D heterometallic structures derived from this two-step strategy are still rare.^{4,5c,d}

Scheme 1. Synthesis of Tetrapyridyl Metalloligands **1** and **2**^a



^aConditions: (i) reflux for 48 h in xylene. Yield = 15% (**1**), 45% (**2**).

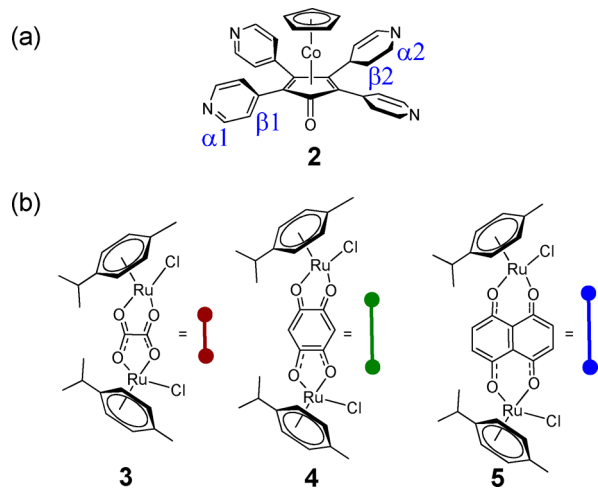
In the latter context, tetrapyridyl “star” connector **1** (Scheme 1) has been studied by several research groups, including us.⁸ Trigonal and tetragonal prismatic cages that are suitable for encapsulation of small molecules have been successfully constructed from this metalloligand. In contrast, metalloligand **2**, which was isolated as the major product in the synthesis of **1** (Scheme 1), has not been studied in self-assembly reactions. In general, the coordination behaviors of such less symmetric ligands are less predictable in self-assembly; thus, they may generate a variety of undesired assemblies upon mixing with metal ions. Despite this inadequacy, they could still be useful for generating 3D supramolecular architectures with diverse sizes and/or topologies. To this end, we herein report the first self-assembly of C_3 -symmetric metalloligand **2** with three

Received: July 21, 2015

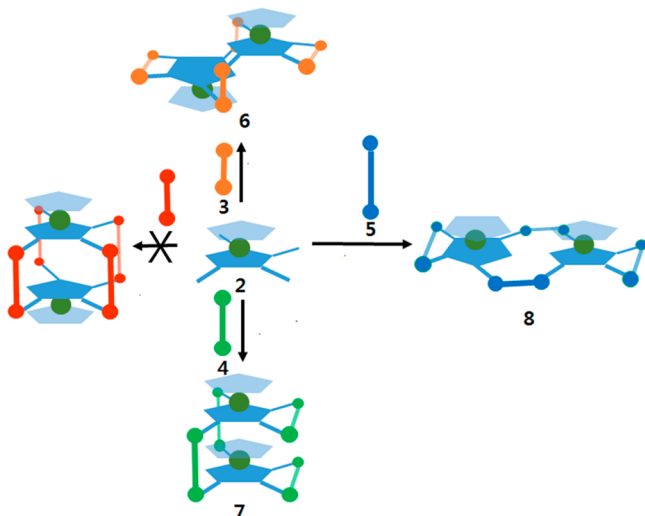
Published: September 8, 2015

different diruthenium acceptors, 3–5 (Chart 1),⁹ that led to the formation of three unique heterometallic A_4D_2 metallacages, 6–8 (Scheme 2).

Chart 1. (a) Tetrapyridyl Electron Donor Molecule 2 and (b) Diruthenium Acceptor Units 3–5 Used in This Study



Scheme 2.



Coordination-driven self-assembly of heterometallic supramolecules 6–8 from tetrapotic metalloligand 2 and diruthenium acceptors 3–5.

RESULTS AND DISCUSSION

Ligand 2 was prepared by adopting a literature procedure, as outlined in Scheme 1, and its molecular structure was determined via single-crystal X-ray diffraction (Figure 1).¹⁰ In the solid state, the cyclopentadiene and cyclopentadienone rings of 2 are separated by ~ 3.33 Å and prefer a nearly eclipsed conformation. The two pyridyl groups near the C=O group, i.e., attached at the 2- and 5-positions of the cyclopentadienone ring (Figure 1), were less twisted (~ 35 and 37°) with respect to the cyclopentadienone ring; in contrast, the other pyridyl units, i.e., the pendants at the 3- and 4-positions, were more twisted, with dihedral angles of ~ 50 and 55° relative to the cyclopentadienone ring. The distance between the nitrogen atoms of the two pyridyl groups located at the 3- and 4-positions is shorter (6.11 Å) than those observed in the other

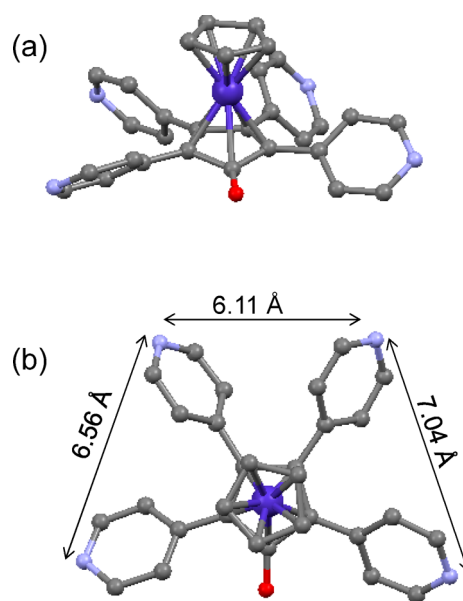
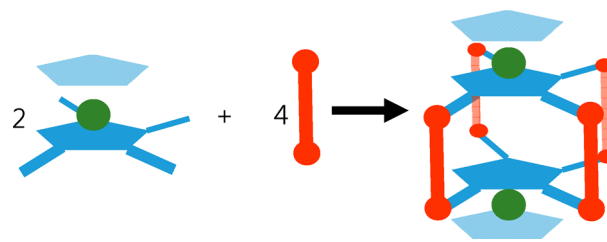


Figure 1. (a) X-ray crystal structure of metalloligand 2. Color code: blue = Co; sky blue = N; red = O; gray = C. H atoms are omitted for clarity. (b) Distances between the pyridyl units in 2.

pairs (6.56 and 7.04 Å). Even though ligand 2 is C_s -symmetric, we expected that we could potentially synthesize octaruthenium tetragonal prismatic structures from the simple reaction of 2 with half-sandwich diruthenium complexes 3–5 in the presence of AgOTf (Scheme 3).

Scheme 3.



Possible coordination-driven self-assembly of a heterometallic tetragonal prism from tetrapotic metalloligand 2.

Syntheses and Spectroscopic Characterization of Supramolecules 6–8. To accomplish the syntheses of the intended tetragonal prismatic structures (Scheme 3), metalloligand 2, diruthenium acceptors 3–5, and AgOTf were mixed in molar ratios of 2:4:8 and stirred at 50 °C for 3 d. Subsequent crystallization of the individual reaction mixtures using a vapor diffusion technique yielded the pure products, 6–8 (Scheme 2.), as evidenced by electrospray ionization mass spectrometry (ESI-MS), ¹H NMR spectroscopy, and X-ray crystallography.

The ¹H NMR spectra together with the ESI-MS data for 6–8 confirmed that, in all cases, the A_4D_2 compositions are present in the solution and gas phases. For example, in the mass spectrum of 6, the presence of peaks at $m/z = 963.91$ and 1335.17 , corresponding to $[M - 4OTf]^{4+}$ and $[M - 3OTf]^{3+}$ (where M = intact assembly), respectively, clearly supports the A_4D_2 self-assembly formation. Similarly for 7, three peaks were found at $m/z = 1014.28$, 1401.73 , and 2176.35 , which correspond to $[M - 4OTf]^{4+}$, $[M - 3OTf]^{3+}$, and $[M - 2OTf]^{2+}$, respectively. Accordingly, the peak at $m/z = 1468.77$,

which corresponds to $[M - 3OTf]^{3+}$, confirmed the A_4D_2 composition of **8**. All these peaks were isotopically resolved and matched very well with their calculated theoretical distributions (see Supporting Information).

Moreover, a single set of signals was observed in the 1H NMR spectra of **6–8**, which provides evidence of their purity. The 1H NMR spectra showed a diagnostic upfield shift of the α -protons (i.e., $\alpha 1$ and $\alpha 2$, Chart 1) in **6–8** as compared to those in free **2** ($\alpha 1$ and $\alpha 2$, $\delta = 8.55$ ppm, Figure 2). For

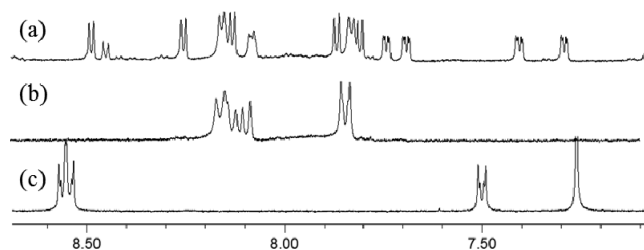


Figure 2. Partial 1H NMR spectra of (a) 2:4:8 mixture of **2**, **4**, and AgOTf at 50 °C after 3 d, (b) metallacage **7**, and (c) metalloligand **2**.

example, in complex **7** (Figure 2b), the signals merged and appeared at $\delta = 8.13$ ppm, while two sets of signals at $\delta = 7.83$ and 8.07 ppm were observed for the two β -protons ($\beta 1$ and $\beta 2$, see Chart 1); these were significantly downfield shifted as compared to those of the free ligand, **2** ($\delta = 7.52$ and 7.06 ppm). The observed upfield shifts of the α -protons and downfield shifts of the β -protons of **7** are similar to those in our recent report on trigonal prismatic cages that were self-assembled from 1,3,5-tris(pyridin-4-ylethynyl)benzene and half-sandwich diruthenium acceptors **3** and **4**.⁶ A comparison of the 1H NMR spectrum of **7** (Figure 2b) with that of the crude reaction mixture (Figure 2a), which contained **2**, **4**, and AgOTf in a 2:4:8 ratio, established that the resonances for complex **7** were present in the reaction mixture; this was also found for complexes **6** and **8**. Therefore, in all three cases, the A_4D_2 species were generated during the self-assembly reactions and isolated via crystallization.

Solid-State Structures. The solid-state structures of complexes **6–8** were established using single-crystal X-ray diffraction. However, the anticipated tetragonal prismatic architectures (Scheme 3.) were not observed in any case. While in the solid state, these supramolecules have A_4D_2 compositions that are similar to those observed in the solution phase (vide supra). The solid-state structures of **6–8** revealed that, in all three cases, two acceptor units intermolecularly linked to the two metalloligand molecules, while each of the other acceptors intramolecularly connected to two adjacent pyridyl units of a metalloligand molecule. Interestingly, the distance between the nitrogen atoms in the adjacent pyridyl groups influences their coordination mode. The two pyridyl units situated at the 3- and 4-positions of the cyclopentadienone ring (Figure 1) were separated by the smallest distances in **6–8**, similar to that observed in metalloligand **2**; thus, they were involved in intramolecular coordination with a diruthenium acceptor.

Moreover, the length of the acceptor unit significantly influences the molecular packing of these metallacages. Thus, supramolecule **6**, which was generated from the self-assembly of ligand **2** and acceptor **3**, adopted a C_{2h} -symmetric waterwheel shape with Ru–N bond distances in the range of 2.10(3)–2.16(3) Å. The metalloligand units in **6** prefer a nearly

staggered conformation of the cyclopentadiene and cyclopentadienone rings (Scheme 2. and Figure 3), and the two C=O groups of the cyclopentadienone rings are arranged in a face-to-face fashion, with a separation between the two cobalt ions of ~ 7.34 Å.

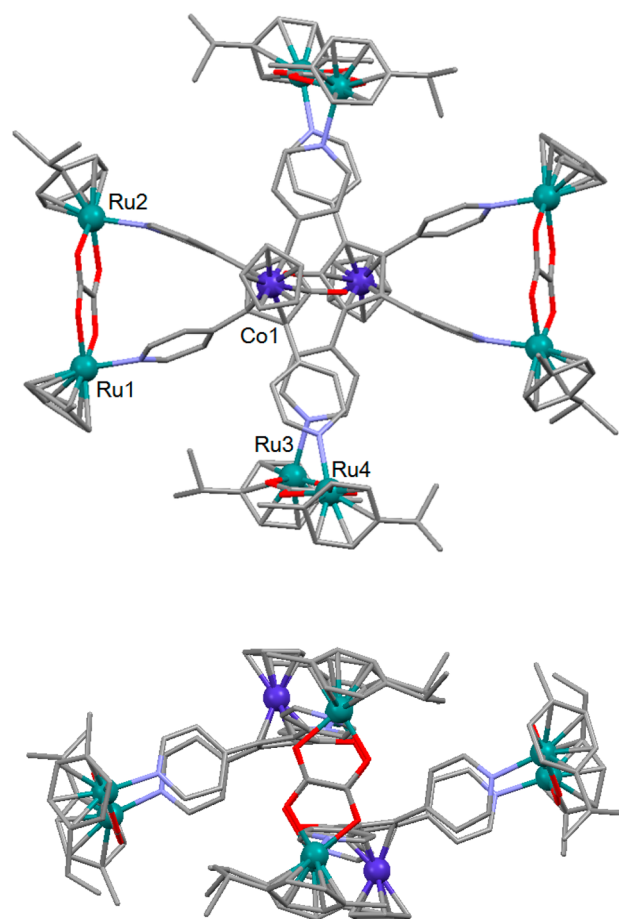


Figure 3. X-ray structure of **6**: top view (top) and side view (bottom). Color code: green = Ru; blue = Co; red = O; sky blue = N; gray = carbon. H atoms and counteranions are omitted for clarity.

A more interesting metallosupramolecular architecture, **7** (Figure 4), was achieved using diruthenium electron acceptor **4**, which has a benzene-1,2,4,5-tetrakis(olate) spacer unit. The Ru–N bond distances in **7** are in the range of 2.093(13)–2.133(15) Å. The structure of complex **7** can be viewed as a molecular tweezer, containing ruthenium–pyridine hinge units, with a distance of ~ 6.98 Å between the two cobalt ions. Because acceptor **4** is longer than acceptor **3**, which has an oxalate bridging unit (Figure 5), two metalloligand units in **7** are located at an optimum distance for π – π stacking interactions between the cyclopentadiene ring of one ligand and cyclopentadienone ring of another metalloligand. We propose that these π – π stacking interactions are responsible for the observed folding in **7**.

Complex **8** also has the same connectivity between ruthenium and pyridine observed in complexes **6** and **7**. However, the structural folding found in complexes **6** and **7** does not occur, and the complex has an unfolded butterfly-like structure, with Ru–N bond distances in the range of 2.09(2)–2.12(2) Å (Figure 6). This suggests that the π – π interactions (vide supra) between two cobalt sandwich metalloligands

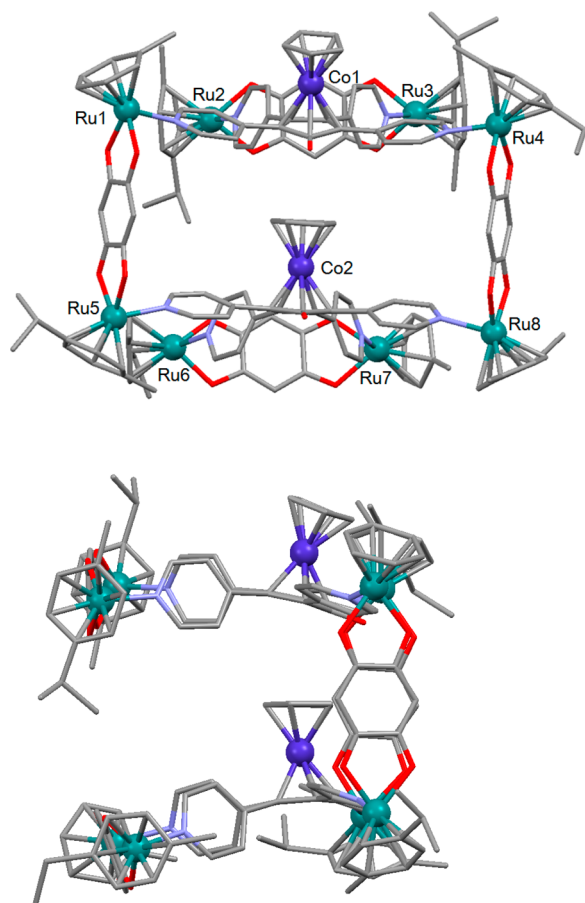


Figure 4. X-ray structure of **7**: side views (top and bottom). Color code: green = Ru; blue = Co; red = O; sky blue = N, gray = carbon. H atoms, isopropyl and methyl groups of *p*-cymene, and counteranions are omitted for clarity.

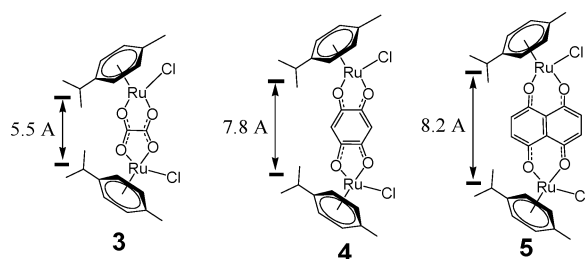


Figure 5. Comparisons of the average distances between the two Ru metal centers in acceptors **3–5**, as observed in the crystal structures of **6–8**.

observed in **7** disappear when acceptor **5**, which has a longer naphthalene-1,4,5,8-tetrakis(olate) spacer, or acceptor **3**, which has a shorter oxalato spacer, is used in the self-assembly.

CONCLUSIONS

In conclusion, we prepared and characterized three unique heterometallic A_4D_2 supramolecular architectures, **6–8**, that self-assembled from C_s -symmetric tetratopic pyridyl metallo-ligand **2** and diruthenium acceptors **3–5**. The purity of these metallosupramolecular assemblies was confirmed by ^1H NMR spectroscopy and ESI-MS, and their solid-state structures were confirmed by X-ray crystallography. Significantly, in the solid state, structural variation of these cages was observed and attributed to the different spacer units of acceptors **3–5**, and

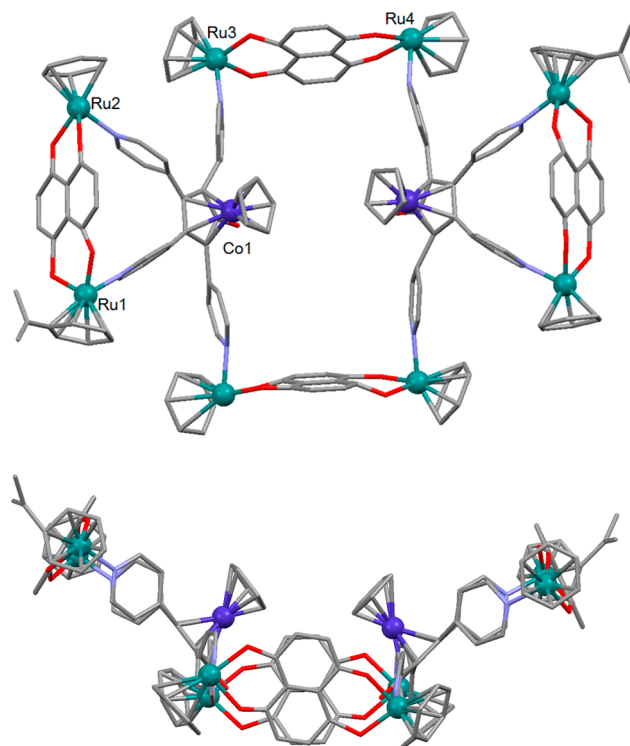


Figure 6. X-ray structure of **8**: top view (top) and side view (bottom). Color code: green = Ru; blue = Co; red = O; sky blue = N; gray = carbon. H atoms, isopropyl and methyl groups of *p*-cymene, and counteranions are omitted for clarity.

thus, waterwheel-shaped (**6**), tweezer-shaped (**7**), and butterfly-shaped (**8**) supramolecular architectures were achieved.

EXPERIMENTAL SECTION

General Considerations. All reagents were anhydrous grade, purchased from Aldrich and TCI, and used without further purification. Column chromatographic separations were performed on silica gel 60 (0.040–0.063 mm), and thin-layer chromatography was performed on silica gel 60F254 plates (Merck). NMR spectra were recorded using a Varian Unity instrument (300 MHz). The ^1H NMR chemical shifts were reported relative to residual solvent signals in parts per million (ppm). ESI-MS was performed using a triple-quadrupole liquid chromatography mass spectrometer (Finnigan TSQ Quantum Ultra EMR) at KBSI Seoul Center. DOSY NMR spectra were recorded using a Bruker instrument at KBSI Gwangju Center.

Synthesis of Tetrapyrrolyl Cobalt Complex 2. 1,2-Di(pyridin-4-yl)ethyne (200 mg, 1.1 mmol), $\text{CpCo}(\text{CO})_2$ (99 mg, 0.55 mmol), and *p*-xylene (20 mL) were placed in a 250 mL round-bottomed flask and refluxed for 48 h under N_2 atmosphere. The reaction mixture was then cooled, and the solvent was evaporated. The solid was chromatographed on silica gel ($\text{CHCl}_3/\text{EtOH} = 10:1$). The isolated product was further chromatographed on silica gel ($\text{CHCl}_3/\text{EtOH} = 20:1$) to obtain the pure product. The product was recrystallized from 1:1 mixture of CHCl_3 and hexane (yield 45%). ^1H NMR (300 MHz, CDCl_3): δ 8.55 [d, 8H, pyridyl (pyr)], 7.52 (d, 4H, pyr), 7.06 (d, 4H, pyr), 5.03 (d, 5H, Cp). IR (KBr disk, cm^{-1}): 1612 (s), 1590 (m), 1408 (w), 844 (w).

Crystal data for 2: triclinic, space group $P\bar{1}$, $a = 11.81025(4)$, $b = 13.0820(4)$, and $c = 13.9126(4)$ Å, $\alpha = 95.332(2)^\circ$, $\beta = 95.332(2)^\circ$, $\gamma = 103.045(2)^\circ$, $V = 1865.31(10)$ Å 3 , $Z = 2$, $F(000) = 810$, $R_1 = 0.0607$, $wR_2 = 0.1621$ for 7568 reflections with $I > 2\sigma(I)$.

Synthesis of Heterometallic Supramolecule 6. Compound **2** (4.0 mg, 7.8 μmol), $[(p\text{-cymene})\text{Ru}_2(\text{oxalato})\text{Cl}_2]$ (9.8 mg, 15.6 μmol), and AgOTf (8.0 mg, 31.2 μmol) were dissolved in nitromethane- d_3 , and the mixture was stirred for 3 d at 50 $^\circ\text{C}$. The

mixture was membrane-filtered. Slow diffusion of diethyl ether into the solution at $-20\text{ }^{\circ}\text{C}$ produced red crystals (yield 43%). $^1\text{H NMR}$ (300 MHz, nitromethane- d_3): δ 1.37 (m, 24H, $-\text{CH}(\text{CH}_3)_2$), 1.45 (m, 24H, $-\text{CH}(\text{CH}_3)_2$), 2.15 (s, 12H, $-\text{CH}_3$), 2.36 (s, 12H, $-\text{CH}_3$), 2.88 (m, 4H, $-\text{CH}(\text{CH}_3)_3$), 3.00 (m, 4H, $\text{CH}(\text{CH}_3)_3$), 5.10 (s, 10H, Cp), 5.73 [t, 16H, *p*-cymene (cym)], 5.90 (m, 16H, cym), 6.01 (t, 8H, pyr), 8.00 (d, 8H, pyr), 8.18 (m, 16H, pyr). Anal. Calcd for $(\text{C}_{156}\text{H}_{154}\text{Co}_2\text{F}_{24}\text{N}_8\text{O}_{42}\text{Ru}_8\text{S}_8 \cdot 5\text{CHCl}_3 \cdot 2\text{MeCN})$: C, 38.62; H, 3.24; N, 2.73. Found: C, 38.60; H, 3.33; N, 2.76. IR (KBr disk, cm^{-1}): 1675 (s), 1410 (w), 1259 (s), 1163 (m), 1031 (s). ESI-MS: 1335.2 (calcd for $[\text{M} - 3\text{OTf}]^{3+}$ 1335.3), 963.9 (calcd for $[\text{M} - 4\text{OTf}]^{4+}$ 963.8).

Crystal data for 6: triclinic, space group $P\bar{1}$, $a = 11.81025(4)$, $b = 13.0820(4)$, and $c = 13.9126(4)$ Å, $\alpha = 95.332^{\circ}$, $\beta = 95.332(2)^{\circ}$, $\gamma = 103.045(2)^{\circ}$, $V = 1865.31(10)$ Å³, $Z = 2$, $F(000) = 810$, $R_1 = 0.0607$, $wR_2 = 0.1621$ for 7568 reflections with $I > 2\sigma(I)$.

Synthesis of Heterometallic Supramolecule 7. Compound 2 (3.0 mg, 5.9 μmol), 4 (7.9 mg, 11.7 μmol), and AgOTf (6.0 mg, 23.4 μmol) were dissolved in MeOH- d_4 in a 5 mL vial. The reaction mixture was stirred for 3 d at $50\text{ }^{\circ}\text{C}$. The mixture was membrane-filtered. Slow diffusion of diethyl ether into the solution at $-20\text{ }^{\circ}\text{C}$ produced red crystals (yield 35%). $^1\text{H NMR}$ (300 MHz, MeOH- d_4): δ 1.26 (d, 24H, $-\text{CH}(\text{CH}_3)_2$), 1.39 (d, 24H, $-\text{CH}(\text{CH}_3)_2$), 2.13 (s, 12H, $-\text{CH}_3$), 2.28 (s, 12H, $-\text{CH}_3$), 2.82 (m, 4H, $-\text{CH}(\text{CH}_3)_2$), 2.98 (m, 4H, $-\text{CH}(\text{CH}_3)_3$), 5.19 (s, 10H, Cp), 5.73 (d, 8H, cym), 5.80 (s, 8H, cym), 5.89 (d, 8H, cym), 5.93 (d, 4H, bq), 6.03 (d, 4H, bq), 6.10 (d, 8H, cym), 7.83 (d, 8H, pyr), 8.07 (t, 8H, pyr), 8.13 (d, 16H, pyr). Anal. Calcd for $(\text{C}_{172}\text{H}_{162}\text{Co}_2\text{F}_{24}\text{N}_8\text{O}_{42}\text{Ru}_8\text{S}_8 \cdot \text{CHCl}_3)$: C, 43.55; H, 3.44; N, 2.35. Found: C, 43.30; H, 3.21; N, 2.22. IR (KBr disk, cm^{-1}): 1523 (s), 1373 (m), 1258 (s), 1159 (m), 1030 (m). ESI-MS: 2176.3 (calcd for $[\text{M} - 2\text{OTf}]^{2+}$ 2176.9), 1401.7 (calcd for $[\text{M} - 3\text{OTf}]^{3+}$ 1401.6), 1014.3 (calcd for $[\text{M} - 3\text{OTf}]^{3+}$ 1014.3).

Crystal data for 7: triclinic, space group $P\bar{1}$, $a = 18.6286(6)$, $b = 22.3857(7)$, and $c = 27.3857(7)$ Å, $\alpha = 70.437(2)^{\circ}$, $\beta = 76.340(2)^{\circ}$, $\gamma = 68.855(2)^{\circ}$, $V = 10002.5(6)$ Å³, $Z = 2$, $F(000) = 4072$, $R_1 = 0.1692$, $wR_2 = 0.3861$ for 38 034 reflections with $I > 2\sigma(I)$.

Synthesis of Heterometallic Supramolecule 8. Diruthenium complex 5 (8.5 mg, 11.7 μmol), AgOTf (6.01 mg, 23.4 μmol), and 2 (3.0 mg, 5.9 μmol) were stirred in nitromethane at $50\text{ }^{\circ}\text{C}$ for 72 h. The reaction mixture was membrane-filtered and recrystallized by diffusion of diethyl ether into a MeOH solution (yield 25%). $^1\text{H NMR}$ (300 MHz, MeOH- d_4): δ 1.26 (d, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.30 (d, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.35 (d, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.38 (d, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.94 (s, 12H, $-\text{CH}_3$), 2.13 (s, 12H, $-\text{CH}_3$), 2.7 (m, 4H, $-\text{CH}(\text{CH}_3)_2$), 2.9 (m, 4H, $-\text{CH}(\text{CH}_3)_2$), 4.95 (s, 10H, Cp), 6.50 (t, 8H, cym), 5.63 (d, 4H, cym), 5.66 (d, 4H, cym), 5.77 (t, 8H, cym), 5.88 (d, 4H, cym), 5.95 (d, 4H, cym), 6.90 (s, 4H, nq), 7.19 (s, 4H, nq), 7.23 (s, 4H, nq), 7.27 (s, 4H, nq), 7.74 (d, 8H, pyr), 7.76 (d, 4H, pyr), 7.78 (d, 4H, pyr), 8.24 (t, 8H, pyr), 8.83 (d, 8H, pyr). Anal. Calcd for $(\text{C}_{188}\text{H}_{170}\text{Co}_2\text{F}_{24}\text{N}_8\text{O}_{42}\text{Ru}_8\text{S}_8 \cdot 3\text{C}_4\text{H}_{10}\text{O})$: C, 47.34; H, 3.97; N, 2.21. Found: C, 47.60; H, 3.80; N, 2.30. IR (KBr disk, cm^{-1}): 1614 (w), 1534 (s), 1275 (s), 1030 (m), 639 (m). ESI-MS: 1468.7 (calcd for $[\text{M} - 3\text{OTf}]^{3+}$ 1468.7).

Crystal data for 8. monoclinic, space group $P2_1$, $a = 27.4515(19)$, $b = 11.2982(10)$, and $c = 37.173(3)$ Å, $\beta = 90.008(5)^{\circ}$, $V = 11529.5(16)$ Å³, $Z = 4$, $F(000) = 6288$, $R_1 = 0.2340$, $wR_2 = 0.5068$ for 11 489 reflections with $I > 2\sigma(I)$.

X-ray Structure Determination. Reflection data for 2 and 6–8 were collected using a Bruker APEX-II CCD-based diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Hemispheres of reflection data were collected as ω scan frames with 0.5° /frame and an exposure time of 10 s/frame. Cell parameters were determined and refined using the SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved using direct methods and refined by full-matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. The crystals of 6–8 diffracted very weakly because of the large amounts of disordered solvents and anions. Geometrical restraints, i.e., DFIX,

SADI, SIMU, and AFIX 66, on part of the hexagonal aromatic rings were used in the refinements.

Some A- and B-level alerts were found using the IUCR's CheckCIF routine for complexes 6–8, all of which originated from the limited diffraction ability of this type of supramolecular compound in the crystal state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07625.

$^1\text{H NMR}$ of 6–8, DOSY NMR spectrum of 7, and ESI-MS spectra of 6–8 (PDF)

Crystallographic data for 2 (CIF)

Crystallographic data for 6 (CIF)

Crystallographic data for 7 (CIF)

Crystallographic data for 8 (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*stang@chem.utah.edu

*leespy@chonnam.ac.kr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.L. acknowledges financial support from the Basic Science Research Program (2014R1A1A1002224) and BRL Program (2015R1A4A1041036) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT, & Future Planning. P.J.S. thanks the NSF (1212799) for financial support.

■ REFERENCES

- (1) (a) Cook, T. R.; Zheng, Y. R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734–777. (b) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (c) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518. (d) Northrop, B. H.; Chercka, D.; Stang, P. J. *Tetrahedron* **2008**, *64*, 11495–11503. (e) Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. *Chem. Rev.* **2015**, *115*, 3012–3035. (f) McConnell, A. J.; Wood, C. S.; Neelakandan, P. P.; Nitschke, J. R. *Chem. Rev.* **2015**, *115*, 7729–7793. (g) Zarra, S.; Wood, D. M.; Roberts, D. A.; Nitschke, J. R. *Chem. Soc. Rev.* **2015**, *44*, 419–432. (h) Saalfrank, R. W.; Maid, H.; Scheurer, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8794–8824. (i) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618–1629. (j) Caulder, D. L.; Bruckner, C.; Powers, R. E.; König, S.; Parac, T. N.; Leary, J. A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 8923–8938. (k) Cook, T. R.; Stang, P. J. *Chem. Rev.* **2015**, *115*, 7001–7045. (l) Ward, M. D.; Raithby, P. R. *Chem. Soc. Rev.* **2013**, *42*, 1619–1636. (m) Safont-Sempere, M. M.; Fernández, G.; Würthner, F. *Chem. Rev.* **2011**, *111*, 5784–5814. (n) Ni, X.-L.; Xue, S.-F.; Tao, Z.; Zhu, Q.-J.; Lindoy, L. F.; Wei, G. *Coord. Chem. Rev.* **2015**, *287*, 89–113.
- (2) (a) Toma, H. E.; Araki, K. *Coord. Chem. Rev.* **2000**, *196*, 307–329. (b) Durot, S.; Taesch, J.; Heitz, V. *Chem. Rev.* **2014**, *114*, 8542–8578. (c) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guillard, R.; Stern, C. *Chem. Rev.* **2009**, *109*, 1659–1713. (d) Pluth, M. D.; Raymond, K. N. *Chem. Soc. Rev.* **2007**, *36*, 161–171. (e) Han, M.; Engelhard, D. M.; Clever, G. H. *Chem. Soc. Rev.* **2014**, *43*, 1848. (f) Newkome, G. R.; Moorefield, C. N. *Chem. Soc. Rev.* **2015**, *44*, 3954–3967. (g) Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243–250.
- (3) (a) Caskey, D. C.; Yamamoto, T.; Addicott, C.; Shoemaker, R. K.; Vacek, J.; Hawkrige, A. M.; Muddiman, D. C.; Kottas, G. S.; Michl, J.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 7620–7628. (b) Yuan, Q.-H.; Yan, C.-J.; Yan, H.-J.; Wan, L.-J.; Northrop, B. H.;

- Jude, H.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 8878–8879.
- (c) Vacek, J.; Caskey, D. C.; Horinek, D.; Shoemaker, R. K.; Stang, P. J.; Michl, J. *J. Am. Chem. Soc.* **2008**, *130*, 7629–7638. (d) Ryu, J. Y.; Lee, J. M.; Park, Y. J.; Nghia, N. V.; Lee, M. H.; Lee, J. *Organometallics* **2013**, *32*, 7272–7274. (e) Wang, M.; Zheng, Y.-R.; Ghosh, K.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 6282–6283. (f) Wang, M.; Zheng, Y.-R.; Cook, T. R.; Stang, P. J. *Inorg. Chem.* **2011**, *50*, 6107–6113.
- (4) (a) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728–1754. (b) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810–6918.
- (5) (a) Zhao, L.; Ghosh, K.; Zheng, Y.-R.; Lyndon, M. M.; Williams, T. I.; Stang, P. J. *Inorg. Chem.* **2009**, *48*, 5590. (b) Zhao, L.; Northrop, B. H.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 11886. (c) Metherell, A. J.; Ward, M. D. *Chem. Commun.* **2014**, *50*, 10979–10982. (d) Reichel, F.; Clegg, J. K.; Gloe, K.; Gloe, K.; Weigand, J. J.; Reynolds, J. K.; Li, C.-G.; Aldrich-Wright, J. R.; Kepert, C. J.; Lindoy, L. F.; Yao, H.-C.; Li, F. *Inorg. Chem.* **2014**, *53*, 688–690.
- (6) Wang, M.; Vajpayee, V.; Shanmugaraju, S.; Zheng, Y.-R.; Zhao, Z.; Kim, H.; Mukherjee, P. S.; Chi, K.-W.; Stang, P. J. *Inorg. Chem.* **2011**, *50*, 1506–1512.
- (7) (a) Lifschitz, A. M.; Rosen, M. S.; McGuirk, C. M.; Mirkin, C. A. *J. Am. Chem. Soc.* **2015**, *137*, 7252–7261. (b) Bloch, E. D.; Britt, D.; Lee, C.; Doonan, C. J.; Uribe-Romo, F. J.; Furukawa, H.; Long, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2010**, *132*, 14382–14384. (c) Son, H.-J.; Jin, S.; Patwardhan, P.; Wezenberg, S. J.; Jeong, N. C.; So, M.; Wilmer, C. E.; Sarjeant, A. A.; Schatz, G. C.; Snurr, R. Q.; Farha, O. M.; Wiederrecht, G. P.; Hupp, J. H. *J. Am. Chem. Soc.* **2013**, *135*, 862–869. (d) Wood, D. M.; Meng, W.; Ronson, T. K.; Stefankiewicz, A. R.; Sanders, J. K. M.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2015**, *54*, 3988–3992. (e) Osuga, T.; Murase, T.; Hoshino, M.; Fujita, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 11186–11189. (f) Brozek, C. K.; Michaelis, V. K.; Ong, T.-C.; Bellarosa, L.; López, N.; Griffin, R. G.; Dincă, M. *ACS Cent. Sci.* **2015**, *1*, 252.
- (8) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401–3412.
- (9) Yan, H.; Suss-Fink, G.; Neels, A.; Stoeckli-Evans, H. J. *Chem. Soc., Dalton Trans.* **1997**, 4345–4350.
- (10) Yuan, Q. H.; Yan, C. J.; Yan, H. J.; Wan, L. J.; Northrop, B. H.; Jude, H.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 8878–8880.