Inorganic Chemistry
Article
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Synthesis and Characterization of Self-Assembled Nanoscopic Metallarectangles Capable of Binding Fullerenes with Size-Selective Responses

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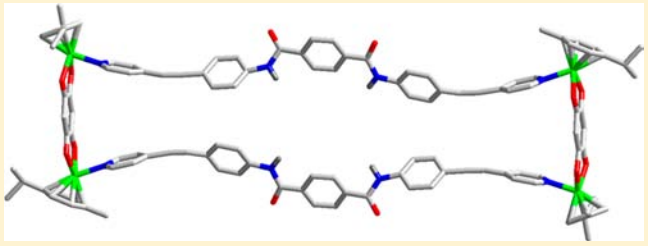
Supporting Information



ABSTRACT: Two new metallarectangles, **4** and **5**, were obtained from the self-assembly of areneruthenium-based molecular clips **2** and **3** with a new dipyridyl donor ligand **1** containing a diamide core and ethynyl spacers. The metallarectangles were characterized by multinuclear NMR, electrospray ionization mass spectrometry, and UV−vis spectroscopy, and the molecular structure of **4** was unambiguously determined by single-crystal X-ray diffraction analysis. Because of the presence of an extended π-electron aromatic surface, the tetracene-containing molecular rectangle **5** was capable of binding C_{60} and C_{70} fullerenes as quantified by UV−vis, emission, and ^{1}H NMR experiments, providing an example of a supramolecular host capable of recognizing large guest molecules.

INTRODUCTION

The formation of new nanoscopic supramolecular coordination complexes (SCCs) via coordination-driven self-assembly has been a cornerstone of the modern supramolecular chemistry commmunity.[1] Over the last 2 decades, an expansive library of SCCs has been filled by various synthetic approaches, ultimately relying on predictable directional interactions between carefully selected metal acceptors and organic donors.[2] Because coordination-driven self-assembly is guided by the structural information encoded in rigid molecular subunits, structures of predetermined shape, size, and functionality may be designed with internal cavities that are capable of encapsulating guest molecules through electrostatic and/or dispersion forces. As such, considerable efforts have been made to develop functional macrocyclic assemblies that show promise in molecular recognition, catalysis, sensing, and photoluminescence, all applications that can utilize host/guest interactions.[3]

Among the suite of metal-containing acceptor building blocks, areneruthenium complexes are especially suitable for use as molecular clips, wherein two Ru centers are bridged by a bis-chelating moiety and capped with a η^6-arene group, leaving a final coordination site to interact with an organic spacer, oftentimes pyridyl-based. Using such acceptors, [2 + 2] metallacycles and [2 + n] prisms may be generated, where n is the number of molecular clips required, as determined by the number of Lewis basic sites of the two donors, which will be held cofacially; a planar tritopic donor (n = 3) will furnish a trigonal prism using three molecular clips.[4] Recently, we reported rigid and shape-persistent [2 + 2] molecular rectangles as host structures for the selective binding of guest molecules of a certain size and shape.[5] Such rectangles are obtained when a molecular clip assembles with a linear ditopic donor, with dimensions determined by the height of the molecular clip and the length of the donor. While a number of such species have been synthesized,[6] elongated structures containing extended linear ligands are relatively rare. Obtaining such ligands through the use of ethynyl spacers is attractive in that the electron-rich π systems that are necessarily present in such designs may endow interesting photophysical properties and rigidity to supramolecules.[7]

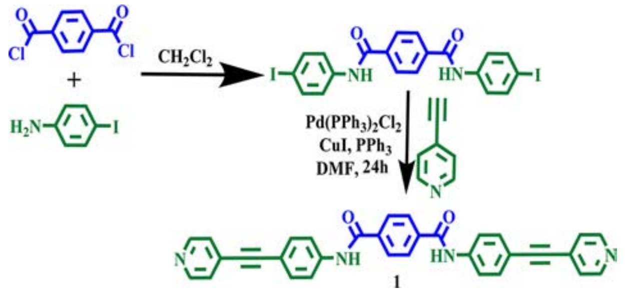
Herein, we report two new large molecular rectangles, **4** and **5**, from the combination of a symmetrically elongated dipyridiyldiethynyl ligand centered on a diamide core with two areneruthenium acceptors. The rectangular nature of these SCCs, the first made using this ligand, was confirmed via X-ray diffraction analysis on a single crystal of **4**. The propensity of both assemblies to form inclusion complexes with large C_{60} and C_{70} guest molecules in solution was demonstrated by absorption and fluorescence quenching experiments. The design of sensing hosts from these discrete rectangles provides a new rationale for the recognition of π-electronic surfaces.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligand. The new *N,N′*-bis[4-(pyridin-4-ylethynyl)phenyl]terephthalamide (**1**) was synthesized in two steps (Scheme 1). The starting ligand precursor *N,N′*-bis(4-iodophenyl)terephthalamide was synthesized by coupling 4-iodoaniline and terephthaloyl dichloride in

Received: March 18, 2013
Published: July 25, 2013

Scheme 1. Synthesis of Ligand 1



CH_2Cl_2 in the presence of triethylamine followed by recrystallization from methanol/H_2O (yield 90%). The resulting product was then used under standard Sonogashira coupling conditions with the hydrochloride salt of 4-ethynylpyridine in *N*,*N*-dimethylformamide (DMF) to generate **1** in ca. 77% overall yield. ^{1}H NMR showed one sharp singlet for the NH at δ 10.81 in dimethyl sulfoxide (DMSO)-d_6, and five aromatic resonances were found, indicating the presence of 20 protons (Figure S2 in the Supporting Information, SI). In the IR spectrum of ligand **1**, the NH and CO vibration stretching peaks for the amide linkage were observed at 3368 and 1692 cm^{-1}, respectively, while the C≡C vibration stretching peak was obtained at 2215 cm^{-1}.

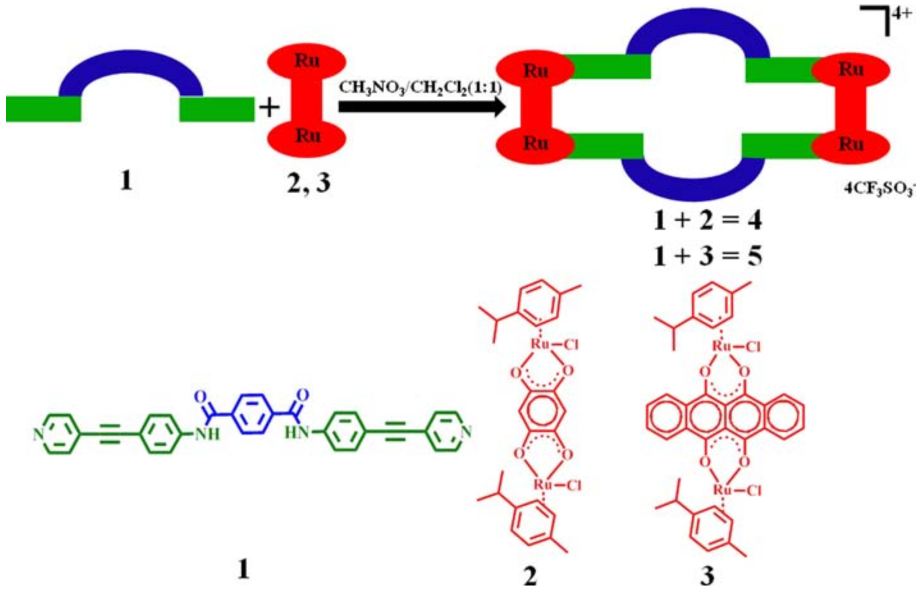
Synthesis and Characterization of Molecular Rectangles. Dinuclear ruthenium complexes [Ru_2(arene)$_2$(OO∩OO)Cl_2] [OO∩OO = 2,5-dihydroxy-1,4-benzoquinonato (**2**) and 6,12-dihydroxytetracene-5,11-dionato (**3**)] were mixed at room temperature in a nitromethane/CH_2Cl_2 (1:1) solution with **1**, and silver triflate furnished metallacycles **4** and **5** as triflate salts with the coformation of silver chloride (Scheme 2). Filtration and precipitation via the addition of diethyl ether yielded **4** and **5** as analytically pure solids.

The ^{1}H NMR spectra of both metallarectangles **4** and **5** clearly showed the formation of a symmetrical species with typical resonance shifts relative to those of the free acceptors due to metal complexation.[7a,8] The CH and Me signals in the ^{1}H NMR spectra of **4** and **5** were shifted downfield about ∼0.5 ppm relative to **2** and **3** in nitromethane-d_3 (Figures S3 and S4 in the SI).

Electrospray ionization mass spectrometry (ESI-MS) spectra of **4** and **5** confirmed the [2 + 2] stoichiometry of the complexes. In the mass spectrum of assembly **4**, peaks at *m*/*z* 801.31 and 563.96 corresponded to the [M − 3OTf]$^{3+}$ and [M − 4OTf]$^{4+}$ charge states (see Figure S5 in the SI), while the spectrum of **5** showed a peak at *m*/*z* 639.62, corresponding to the [M − 4OTf]$^{4+}$ charge state (see Figure S6 in the SI). These peaks were all isotopically resolved and matched well with their theoretical isotopic distributions.

The molecular structure of **4** was unequivocally determined by single-crystal X-ray diffraction analysis. A single crystal suitable for X-ray diffraction was obtained by the slow vapor diffusion of diethyl ether into a nitromethane/methanol (1:1) solution of **4**. As expected, the molecular structure of **4** included a large cavity (8.5 × 32.43 Å^2), as shown in Figure 1. Two dipyridyl ligands bridge two [Ru_2(arene)$_2$(2,5-dihydroxy-1,4-benzoquinonato)$_2$]$^{4+}$ building blocks to form a [2 + 2] M_4L_2 rectangle. Each cymene-capped ruthenium coordination sphere was further coordinated by a N atom from the ditopic ligand and two O atoms from the bridging moiety. The Ru−$N_{pyridine}$ bond distances were ∼2.019 Å, comparable to the distances found within other tetracationic rectangles.[5,6] The central diamide cores of the ligands were oriented such that the NH groups were directed inward, with the carbonyls directed away from the internal cavity. The distance between the opposing carbonyls was ∼11.12 Å, while the NH groups were held closer at ∼6.57 Å. The extended nature of the ditopic ligand results in a 32.43 Å separation between the two ruthenium-based acceptors, with an 11.12 Å spacing between ligands. In the solid state, two triflate anions occupy the internal cavity bound through weak hydrogen-bonding interactions (Figure S7 in the SI). The hydrogen-bonding distances between the H atoms of the amide groups (NH) and the O atoms of the triflate anion were in the range of 2.18−3.03 Å for **4**.

Scheme 2. Synthesis of Nanoscopic Metallarectangles



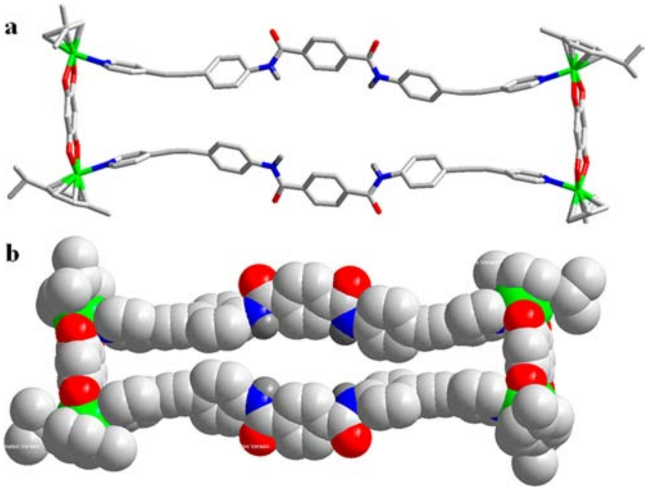


Figure 1. Crystal structure of **4**. (a) Schematic diagram showing the two Ru^{2+} ions (green) coordinated by four pyridine N atoms (blue). (b) Side view shown as a space-filling model. The triflate anion and solvent molecules are omitted for clarity.

Absorption and Emission Studies. The electronic absorption spectra of **4** and **5**, along with their corresponding metal acceptors (**2** and **3**) were investigated in methanol solutions at 1×10^{-5} M (Figure 2). The absorption spectra exhibit bands at λ_{abs} = 502 nm for **4** and λ_{abs} = 526, 565, and 610 nm for **5**. The dinuclear areneruthenium acceptors also exhibited energy absorption bands at 485 nm and 521, 553, and 599 nm for **2** and **3**, respectively. These bands are likely a combination of intra/intermolecular $\pi \rightarrow \pi^*$ transitions mixed with metal-to ligand charge-transfer transitions. As such, these areneruthenium-based bands are also preserved upon self-assembly, giving rise to strong absorption for **4** and **5**. Rectangle **4** gives a strong absorption band red-shifted with respect to acceptor **2** by ~17 nm. Similar red shifts are observed for bands in **5** that correspond to absorption in donor **3**.

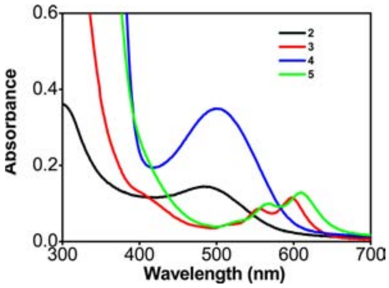


Figure 2. Electronic absorption spectra of **2**–**5** in methanol (1×10^{-5} M).

The metallarectangle **5** exhibits fluorescence emission at 530 and 570 nm upon photoexcitation at 390 nm. This fluorescence originated from the acceptor because the emission wavelengths matched well with the emission bands observed for the acceptor alone (Figure 3). The emission intensity of **5** was notably quenched compared with the acceptor **3**. The intramolecular photoinduced electron transfer in **5** from the acceptor **3** to the donor **1** could be responsible for the observed emission quenching.[5]

Fullerene Binding Studies. One of the major motivations for constructing such rigid, ethynyl-containing metallacycles was to develop a novel class of fullerene receptors, which could bind strongly and efficiently with potential size selectivity, in analogy to known porphyrin-containing covalent macrocycles[9] and supramolecular cages,[10] which exhibit strong binding interactions. Given the extended π systems of these rectangles and the suitable dimensions revealed from the structural studies of **4**, interactions with fullerenes were expected. Because the tetracene bridging moiety of **5** resulted in easily monitored photophysical properties, it was selected for titrations with C_{60} and C_{70} using UV–vis absorption and fluorometric methods in a 1,1,2,2-tetrachloroethane (TCE) solution. Upon the gradual addition of C_{60} to a solution of **5** in TCE, the intensity of the absorption peaks of **5** at 277 and 332 nm increased (Figure 4).

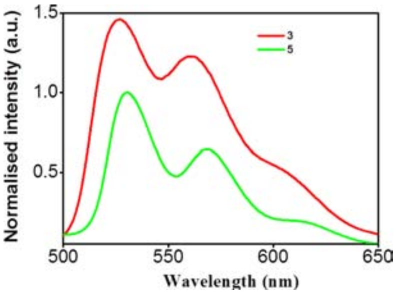


Figure 3. Normalized emission spectra of **3** and **5** in methanol (1×10^{-5} M).

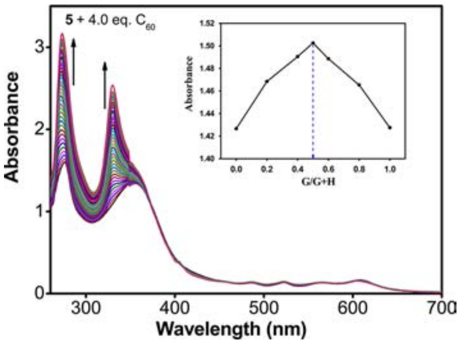


Figure 4. Changes in the absorption spectra of **5** in a TCE solution (1×10^{-5} M) upon the addition of 4.0 equiv of C_{60} in a TCE solution (1×10^{-4} M). Inset: Job's plot of metallarectangle **5** with C_{60} in a TCE solution.

A similar trend in the UV–vis titration curve at 277 and 332 nm was observed when a solution of **5** in TCE was titrated with C_{70} (Figure 5). According to the Job plot, **5** formed a 1:1 host/guest complex with C_{60} (see the inset in Figure 4) and C_{70} (see the inset in Figure 5), respectively.

Additional evidence in support of C_{60} and C_{70} binding with **5** came from fluorescence titration experiments. The ethynyl-containing donors with areneruthenium acceptors make **5** particularly electron-rich, which was manifested in strong fluorescence emission centered at 527 and 560 nm (Figure 3). The assembly **5** was titrated with incremental amounts of C_{60} and C_{70} in a TCE solution. The change in the fluorescence intensity at 527 nm was monitored with the 390 nm excitation at which the change in the molar absorption of the host/guest solution is marginal during titration. As shown in Figures 6 and 7, the emission intensity of **5** gradually decreased upon the addition of C_{60} and C_{70}, respectively. Because both C_{60} and C_{70} were nonemissive at the same excitation, such changes in the

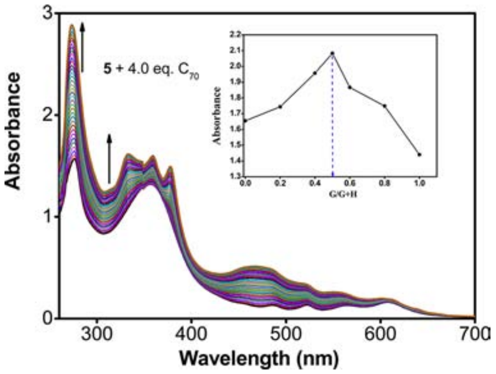


Figure 5. Change in the absorption spectra of **5** in a TCE solution (1×10^{-5} M) upon the addition of 4.0 equiv of C_{70} in a TCE solution (1×10^{-4} M). Inset: Job's plot of metallarectangle **5** with C_{70} in a TCE solution.

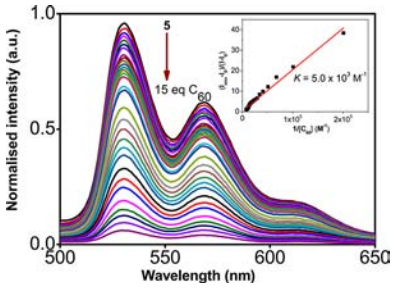


Figure 6. Changes in the emission spectra of **5** in a TCE solution (1×10^{-5} M) upon the addition of 15 equiv of C_{60} in TCE (1×10^{-3} M; λ_{exc} = 390 nm).

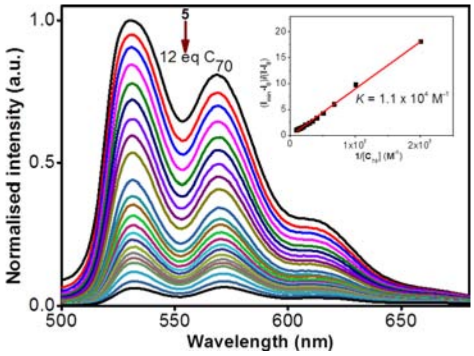


Figure 7. Changes in the emission spectra of **5** in a TCE solution (1×10^{-5} M) upon the addition of 12 equiv of C_{70} in TCE (1×10^{-3} M; λ_{exc} = 390 nm).

emission intensity were consistent with the formation of a charge-transfer inclusion complex between the metallacyclic host and C_{60} or C_{70}.[11]

Furthermore, the association constants of **5** were estimated from the fluorescence intensity changes using Benesi–Hildebrand analysis,[12] which afforded *K* values of 5.0×10^3 M^{-1} for C_{60} and 1.1×10^4 M^{-1} for C_{70} (insets in Figures 6 and 7). It may be noted though that the *K* values could not be adequately approximated from the absorption titration because of large absorption by free C_{60} and C_{70} guests. The observed *K* values further indicate that the binding ability of **5** with C_{70} is better than that with C_{60}.

In order to further understand the binding interaction of **5** with fullerenes, the binding was also examined by ^1H NMR spectroscopy: a 1:1 mixture solution of **5** and C_{60} in TCE-d_2 showed significant shifts of the proton resonances for the donor ligand that are distinctly different from the signals of free rectangle **5**. This result confirms the binding interaction between C_{60} and metallarectangle **5** (Figure 8).

■ CONCLUSION

In conclusion, we report the syntheses of two new self-assembled metallarectangles, **4** and **5**, with adaptable cavities via new *π*-electron-rich *N*,*N*′-bis[4-(pyridin-4-ylethynyl)phenyl]-terephthalamide donor **1** and areneruthenium acceptors **2** and **3**. The formation of both molecular rectangles was established by various spectroscopic techniques, and the molecular structure of metallarectangle **4** was determined by single-crystal X-ray diffraction analysis. Because of its extended aromatic surface, metallarectangle **5** was capable of interacting with C_{60} and C_{70}, providing a basis for host/guest chemistry using SCCs with large substrates by exploiting *π* interactions. Currently, the binding behavior and charge-transfer chemistry of such metallarectangles with higher-order fullerenes are being investigated and will be reported in due course.

■ EXPERIMENTAL SECTION

Materials and Methods. All chemicals used in this work were purchased from commercial sources and used without further purification. Starting areneruthenium chlorides were prepared as previously described.[13,14] ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. ^1H NMR chemical shifts are reported relative to residual solvent signals. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using ESI running the *MassLynx* software suite. IR spectra (in KBr pellets) were recorded using a Varian 2000 FTIR spectrometer. Elemental analyses were performed using an Elemental GmbH Vario EL-3 instrument. Absorption spectra were recorded using a CARY 100 Conc UV–vis spectrophotometer. Fluorescence titration studies were carried out on a Horiba FluoroMax-4 fluorimeter.

UV–Vis Binding Study. A stock solution of **5** in a TCE solution (2.0 mL, 1×10^{-5} M) was prepared and placed in a quartz cell. Stock solutions (1×10^{-4} M) of the corresponding fullerenes in TCE were added incrementally, and the absorption spectra were recorded at room temperature.

Fluorescence Sensing Study. A 2 mL stock solution (1×10^{-5} M) of metallacycle **5** was placed in a 1-cm-wide quartz cell, and C_{60} and C_{70} stock solutions (1×10^{-3} M) were added incrementally. Titration experiments were carried out at 298 K, and each measurement was repeated at least three times to acquire concordant values. Both the excitation and emission slits were 5 nm. An excitation wavelength (λ_{exc}) of 390 nm for **5** was used for all measurements, and emission was monitored at 527 nm. The association constant (*K*) was estimated from the change in the emission intensity using Benesi–Hildebrand analysis; the insets in Figures 6 and 7 are plots of $(I_{min} - I_0)/(I - I_0)$ vs $1/[G]$, where I_0 is the fluorescence intensity of the host, I is the observed intensity, I_{min} is the lowest intensity, and G is C_{60} or C_{70}.

Crystallographic Data Collection and Refinement of Metallacycle 4. A crystal of **4** was coated with paratone oil, and diffraction data were measured at 173 K with Mo K*α* radiation on an X-ray diffraction camera system using an imaging plate equipped with a graphite crystal incident beam monochromator. *RapidAuto* software[15] was used for data collection and data processing. The structure was solved by the direct methods and was refined by full-matrix least-squares calculation with the *SHELXTL* software package.[16] One ligand, two Ru atoms, two *p*-cymene ligands, two triflate anions, and a lattice water molecule were observed in the asymmetric unit cell. All non-H atoms were refined anisotropically; the H atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C,N)$ and

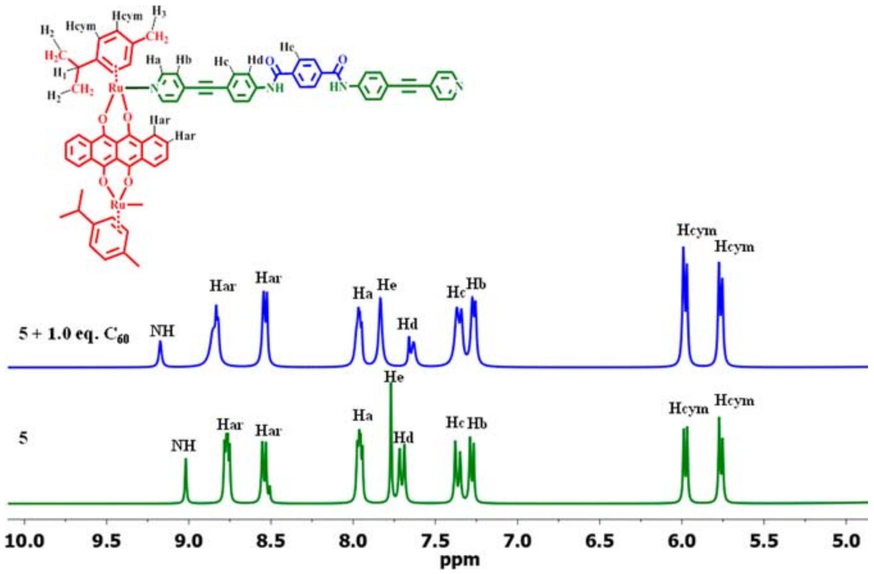


Figure 8. Comparative ^{1}H NMR spectra of **5** and **5** + C_{60} in a TCE-d_2 solvent.

$1.5U(C_{\text{methyl}})$, and their coordinates were allowed to reside on their respective atoms. H atoms attached to the lattice water molecule were not included in the least-squares refinement. The least-squares refinement of the structural model was performed under the geometry constraint AFIX for phenyl and pyridyl portions of the ligand and under geometry restraints and displacement parameter restraints such as DFIX, DANG, and ISOR. Refinement of the structure converged at final R1 = 0.1819 and wR2 = 0.4658 for 2992 reflections with $I > 2\sigma(I)$ and R1 = 0.2392 and wR2 = 0.4952 for all 5365 reflections. The largest difference peak and hole were 1.902 and −0.707 e Å^{-3}, respectively.

Synthesis of *N,N*′-Bis(4-iodophenyl)terephthalamide. A solution of terephthaloyl dichloride (1 g, 4.90 mmol) and triethylamine (3 mL) in 20 mL of CH_2Cl_2 was prepared and chilled to 4 °C in an ice bath for 5 min, and then 4-iodoaniline (2.26 g, 10.30 mmol) was added slowly to the cold solution over a period of 10 min. The reaction mixture was stirred at room temperature overnight. The resulting precipitate was collected on a frit, recrystallized with MeOH/H_2O, and dried in a vacuum oven. Yield: ca. 90% (2.60 g). Anal. Calcd for $C_{20}H_{14}I_2N_2O_2$: C, 42.28; H, 2.48; N, 4.93. Found: C, 42.08; H, 2.26; N, 4.50. ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm): 10.50 (s, 2H, CONH), 8.08 (d, 4H, H_c), 7.70−65 (d, 8H, H_a/H_b).

Synthesis of Ligand *N,N*′-Bis[4-(pyridin-4-ylethynyl)phenyl]-terephthalamide (1). In a flame-dried Schlenk flask, 4-ethynylpyridine hydrochloride (0.615 g, 4.4 mmol) and triethylamine (10 mL) were vigorously stirred for 30 min. During this time, a white precipitate formed. Next, DMF (30 mL), $Pd(PPh_3)_2Cl_2$ (0.062 g, 0.09 mmol), PPh_3 (0.024 g, 0.09 mmol), CuI (0.018 g, 0.09 mmol), and H_2I (1.0 g, 1.76 mmol) were successively added. The Schlenk flask was wrapped in aluminum foil to keep the reaction mixture in the dark. The reaction mixture was refluxed for 24 h at 80 °C. The resulting brown mixture was filtered on a frit, the solvent was removed, and the residue was recrystallized with CH_3OH/H_2O (1:1). The compound was filtered and dried under vacuum. Yield: ca. 77% (0. 700 g). Anal. Calcd for $C_{34}H_{22}N_4O_2$: C, 78.75; H, 4.28; N, 10.80. Found: C, 78.62; H, 4.21; N, 10.69. IR (KBr, ν, selected peaks): 3368 (NH), 2215 (C≡C), 1692 (C═O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm): 10.67 (s, 2H, CONH), 8.62 (d, 4H, J = 4.8 Hz, H_a), 8.11 (s, 4H, H_e), 7.93 (d, 4H, J = 8.7 Hz, H_d), 7.64 (d, 4H, J = 8.4 Hz, H_c), 7.52 (d, 4H, J = 5.4 Hz, H_b).

Synthesis of Metallacycle 4. A mixture of starting complex **2** (0.0068 g, 0.01 mmol) and 2 equiv of $AgCF_3SO_3$ (0.0052 g, 0.02 mmol) in nitromethane/CH_3OH (4 mL, 1:1) was stirred at room temperature for 2 h and filtered to remove AgCl. The corresponding donor ligand **1** (0.0052 g, 0.01 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 12 h, and the solvent was removed under reduced pressure. The crude product thus obtained was redissolved in nitromethane/CH_3OH (10 mL, 1:1) and subjected to vapor diffusion of diethyl ether. This resulted in a highly red crystalline product within 1 week.

Yield: ca. 90%. Anal. Calcd for $C_{124}H_{104}F_{12}N_8O_{24}Ru_4S_4$: C, 52.24; H, 3.68; N, 3.93. Found: C, 52.18; H, 3.70; N, 3.90. FTIR (KBr, ν, selected peaks): 3341 (NH), 2241 (C≡C), 1632 (C═O) cm^{-1}. ESI-MS peaks at m/z 801.31 and 563.96 corresponding to $[M - 3OTf]^{3+}$ and $[M - 4OTf]^{4+}$ charge states. respectively. ^{1}H NMR (nitromethane-d_3, 300 MHz, δ, ppm): 9.06 (s, 4H, CONH), 8.22 (d, 8H, J = 6.6 Hz, H_a), 7.82 (s, 8H, H_e), 7.57 (d, 8H, J = 9.0 Hz, H_d), 7.47−7.43 (m, 16H, H_b/H_c), 5.98 (d, 8H, J = 6.3 Hz, $-C_6H_4$), 5.77−5.75 (m, 12H, $-C_6H_4$/bz), 2.98−2.86 (m, 4H, $-CH(CH_3)_2$), 2.22 (s, 12H, $-CH_3$), 1.36 (d, 12H, $-CH(CH_3)_2$).

Synthesis of Metallacycle 5. A mixture of starting complex **3** (0.0083 g, 0.01 mmol) and 2 equiv of $AgCF_3SO_3$ (0.0052, 0.02 mmol) in 6 mL of methanol was stirred at room temperature for 2 h and filtered to remove AgCl. The corresponding donor ligand **1** (0.0052 g, 0.01 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 6 h, and the solvent was removed under reduced pressure. The crude product was redissolved in nitromethane and subjected to vapor diffusion of diethyl ether. This resulted in a highly crystalline product. The product was filtered and dried under vacuum. Yield: ca. 90%. Anal. Calcd for $C_{148}H_{116}F_{12}N_8O_{24}Ru_4S_4$: C, 56.41; H, 3.71; N, 3.56. Found: C, 56.60; H, 3.73; N, 3.45. FTIR (KBr, ν, selected peaks): 3349 (NH), 2242 (C≡C), 1629 (C═O) cm^{-1}. ESI-MS peaks at m/z 639.62 corresponding to the $[M - 4OTf]^{4+}$ charge state. ^{1}H NMR (nitromethane-d_3, 300 MHz, δ, ppm): 9.01 (s, 4H, CONH), 8.76 (d, 8H, J = 6.6 Hz, H_{ar}), 8.54 (d, 8H, J = 6.6 Hz, H_{ar}), 7.96 (d, 8H, J = 6.6 Hz, H_a), 7.76 (s, 8H, H_e), 7.69 (d, 8H, J = 8.7 Hz, H_d), 7.36 (d, 8H, J = 8.7 Hz, H_c), 7.27 (d, 8H, J = 6.6 Hz, H_b), 5.97 (d, 8H, J = 6.3 Hz, $-C_6H_4$), 5.76 (d, 8H, J = 6.3 Hz, $-C_6H_4$), 3.09−3.04 (m, 4H, $-CH(CH_3)_2$), 2.30 (s, 12H, $-CH_3$), 1.39 (d, 12H, $-CH(CH_3)_2$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra of the starting precursor and ligand **1** and of **4** and **5** in nitromethane-d_3, ESI-MS of both metallarectangles, an ORTEP diagram of metallarectangle **4**, and a table of bond lengths and angles for **4**. 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.

■ ACKNOWLEDGMENTS

This work was supported by the Basic Science Research program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, and Future Planning (Grant NRF-2013R1A1A2006859). A Priority Research Centers program (2009-0093818) through the NRF is also financially appreciated. X-ray diffraction experiments using synchrotron radiation were performed at the Pohang Accelerator Laboratory in Korea. We thank Prof. Peter J. Stang, Department of Chemistry, University of Utah, for help with ESI-MS experiments.

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