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# Decorating Diruthenium Compounds with Fréchet Dendrons via the *Click* Reaction

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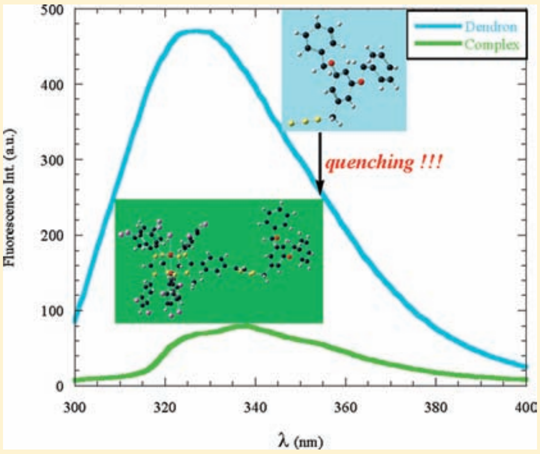
S *Supporting Information*

**ABSTRACT:** A series of dendronized-$Ru_2$ compounds were prepared using the Cu(I)-catalyzed 1,3-dipolar cycloaddition (*click* reaction) between the terminal azides of azidopoly(benzyl ether) dendrons ($[D_n]$-$N_3$, $n = 0-3$) and $Ru_2$ units bearing one or two terminal ethynes, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(DMBA\text{-}4\text{-}C_2H)_mCl$ with $m = 1$ and 2, and D(3,5-$Cl_2$Ph)F and DMBA-4-$C_2$H as *N,N*′-bis(3,5-dichloro-phenyl)formamidinate and *N,N*′-dimethyl-4-ethynylbenzamidinate, respectively. The resultant $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(DMBA\text{-}D_n)_mCl$ compounds were further functionalized by the axial ligand displacement of Cl by -$C_2$Ph to yield new compounds $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(DMBA\text{-}D_n)_m(C_2Ph)_2$ (where $m = 1$ and 2; $n = 0$ and 1). All $Ru_2$ compounds reported herein were analyzed via mass spectrometry, voltammetry, and UV−visible and fluorescence spectroscopy. Density-functional theory (DFT) calculations were performed on a model compound to gain more insight into the molecular orbital energy levels possibly associated with the photophysical data obtained and presented herein.



## INTRODUCTION

The study of metallodendrimers has been topical in recent years because of the rich topological features and versatile materials properties achieved upon the introduction of metal centers.[1,2] Metallodendrimers are currently investigated for applications such as catalysts,[3] nonlinear optical chromophores,[4] and drug delivery.[5] Metal centers may function as connectors, branching points, or terminal (surface) centers, and can be located at either specific or random loci within dendritic architectures.[1] While metallodendrimer research has been dominated by monometallic species,[6] those based on bimetallic species have been explored by Luck and Liwporncharoenvong,[7] Liu et al.,[8] Deschenaux et al.,[9] and us.[10] The recent success in ligand modification on the periphery of diruthenium compounds has provided easy access for functionalizing $Ru_2$ units with a variety of functional groups including terminal alkynes and olefins,[11−13] and the presence of these reactive functional groups provides venues for further covalent modifications. During the recent years, diruthenium (II,III) and (III,III) species have been shown to exhibit interesting molecular magnetism,[14,15] molecular wire characteristics,[16] and reactivity such as C−H activation[17] and sulfur oxygenation.[18] We hope to further improve the chemical and physical properties of diruthenium species by attaching dendrons through the Cu(I) catalyzed 1,3-dipolar cycloaddition reaction (*click* reaction) with benzyl azide.[19]

Since its reintroduction by Meldal et al.[20] and Sharpless et al.,[21] the *click* reaction has enjoyed great successes in polymer and materials syntheses.[22] Our laboratory has been exploring the utility of the *click* reaction in expeditious synthesis of photoactive dendrimers. Previously we communicated the monosubstitution of azidopoly(benzyl ether) dendrons (Fréchet type, Chart 1)[23] to diruthenium compounds via the *click* reaction. In this contribution, we report the synthesis and characterization of a novel series of mono- and di- substituted $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(DMBA\text{-}D_n)_mCl$ ($m = 1$ or 2; $n = 0-3$) complexes prepared from the Cu(I)-catalyzed 1,3-dipolar cycloaddition between a $Ru_2$ complex containing one and two terminal ethynes (Scheme 1) and azidopoly(benzyl ether) dendrons ($[D_n]$-$N_3$, $n = 0-3$) (Chart 1). These compounds have been characterized with techniques including UV−vis spectroscopy, X-ray crystallography, voltammetry, photoluminescence, high-resolution mass spectrometry (HR-MS), and density-functional theory (DFT) calculations.

## RESULTS AND DISCUSSION

**Synthesis.** *$Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_n)Cl$ ($n = 0-3$, Scheme 1).* The synthetic methods for diruthenium compounds of a set of mixed bridging bidentate ligands have been developed by the laboratories of Cotton,[24] Jiménez-Aparicio,[14,25] and Ren.[12,26] The initial attempt at peripheral modification via the *click* reaction was the reaction between $[D_1]$-$N_3$ and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)Cl$ (**1**), where D(3,5-$Cl_2$Ph)F and DMBA-4-$C_2$H are respectively *N,N*′-bis(3,

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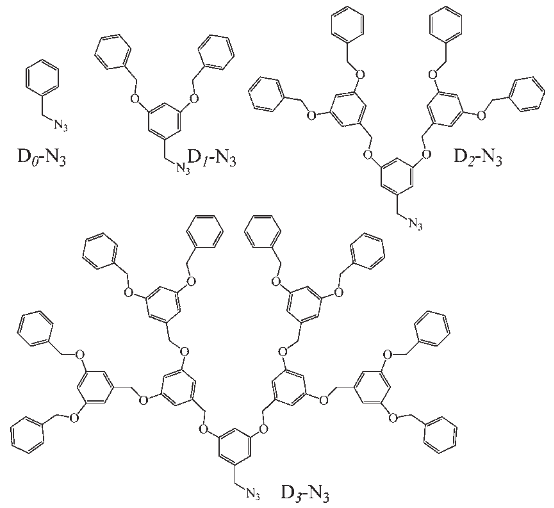
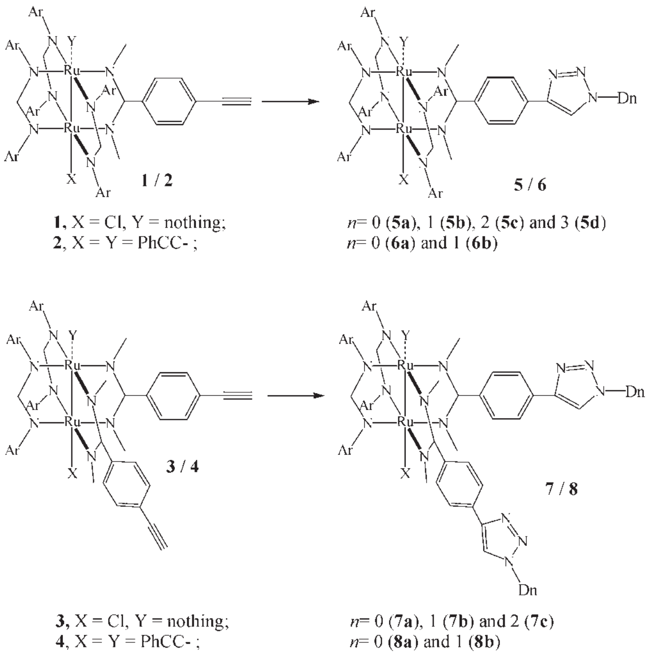
Chart 1. Azido Containing Poly(benzylether) Dendrons



Scheme 1. Synthesis of $Ru_2$-Containing Dendrimers (Ar = 3,5-$Cl_2$phenyl)



**1**, X = Cl, Y = nothing;
**2**, X = Y = PhCC- ;

$n$= 0 (**5a**), 1 (**5b**), 2 (**5c**) and 3 (**5d**)
$n$= 0 (**6a**) and 1 (**6b**)

**3**, X = Cl, Y = nothing;
**4**, X = Y = PhCC- ;

$n$= 0 (**7a**), 1 (**7b**) and 2 (**7c**)
$n$= 0 (**8a**) and 1 (**8b**)

5-diclorophenyl)formamidinate and $N$,$N'$-dimethyl-4-ethynylbenzamidinate. In the presence of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate, the terminal azide of the dendron underwent the *click* reaction with the terminal alkyne of the $Ru_2$ complex (Scheme 1). The solvent combination of $^tBuOH/H_2O$ in a 2:1 ratio, optimized in our early study,[10] resulted in a slow and incomplete reaction. However, the use of $THF/H_2O$ (2:1) afforded the anticipated $Ru_2$-$[D_1]$ *click* product **5b** in a 91% yield. Similar *click* reactions with both lower ($[D_0]$-$N_3$) and higher generation dendrons ($[D_2]$-$N_3$ and $[D_3]$-$N_3$) proceeded under the same conditions to give compounds **5a**, **5c**, and **5d** with yields of 23, 77, and 51%, respectively. The purification of compounds **5a**−**5d** was achieved via simple extraction with $CH_2Cl_2$ from the reaction mixture followed by subsequent flash silica chromatography. The relatively low yield of the $Ru_2[D_0]$-*click* product is likely due to the oily nature of the $[D_0]$-$N_3$ dendron, as opposed to the fact that the latter generation dendrons were isolated as white crystalline solids. The high-spin nature ($S = 3/2$) of the monosubstituted $Ru_2[D_n]$-*click* complexes ($n = 0-3$) prevents analysis by $^1H$ NMR spectroscopy, but they were authenticated using nano-electrospray ionization (nESI) mass spectrometry, and were further analyzed via cyclic voltammetry and UV-vis-NIR spectroscopy. The structure of compound **5b** was established through X-ray crystallographic studies as described below.

*$Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_n)(C_2Ph)_2$ (n = 0 and 1).* Compound **1** reacted with 10 equiv of LiC≡CPh to yield its bis(phenylacetylide) derivative **2** under conditions previously established for similar $Ru_2$ compounds.[13] Compounds **6a** and **6b** were prepared from **2** under the same *click* conditions previously stated for the monosubstituted complexes and were isolated in 24 and 52%, respectively. Once again, the relatively low yield of **6a** is primarily due to the oily nature of $[D_0]$-$N_3$. The monosubstituted bis(phenylacetylide) *click* complexes (**6a** and **6b**) are diamagnetic, which enables their characterization via $^1H$ NMR spectroscopy. The complexes were further analyzed via nESI mass spectrometry, cyclic voltammetry, and UV-vis-NIR spectroscopy.

*cis-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_n)_2Cl$ (n = 0−2).* Dendritic modification of $Ru_2$ compounds (**3** and **4**) containing two terminal ethynes via the *click* reaction was also investigated. The previous reaction based on *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2Cl$ (**3**) only led to a mixture of unidentifiable products.[10] The failed reaction may be attributed to either the labile nature of the axial chloro ligand in $Ru_2(DArF)_2(DMBA)_2$-type compounds, which enables the starting compound to undergo several different reactions under the *click* conditions, or a simple experimental error during the preliminary study. Nevertheless, we have had more successes in the current study: the *click* reactions between compound **3** with $[D_n]$-$N_3$ ($n = 0-2$) to yield **7a** (84%), **7b** (51%), and **7c** (57%), respectively. While the reactions yielding **7a** and **7b** proceeded with ease, the formation of **7c** was achieved in a stepwise fashion. Simply reacting **3** with 2.2 equiv of $[D_2]$-$N_3$ did not yield the desired disubstituted product, but rather the monosubstituted product that was identified by nESI-MS. Reacting the monosubstituted product with another 2.2 equiv of $[D_2]$-$N_3$ resulted in the formation of **7c** in a relatively good yield. On the other hand, several attempts of the *click* reaction between compound **3** and $[D_3]$-$N_3$ only yielded the monosubstituted $[D_3]$-$N_3$ *click* product, and further reaction of the monosubstituted product with an additional 2.2 equiv of the dendron did not yield the desired *cis*-$Ru_2[D_3]$ *click* product. Both the stepwise attachment of $[D_2]$-$N_3$ and the unsuccessful attachment of the second $[D_3]$-$N_3$ reflect the decreasing reactivity with the increasing bulkiness of Fréchet dendrons.

*cis-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_n)_2(C_2Ph)_2$ (n = 0 and 1).* The *click* reaction between compound **4** ($Ru_2$(III,III)) and 2.2 equiv of either $[D_0]$-$N_3$ or $[D_1]$-$N_3$ successfully yielded **8a** or **8b**, respectively. The products were isolated in 46% (**8a**) and 57% (**8b**) yields, and their identities authenticated via nESI-MS and $^1H$ NMR.

*Molecular Structure of **5b**.* Single crystals of X-ray quality were grown by slow evaporation of a THF/hexanes solution of **5b**. The structural plot of **5b** is shown in Figure 1, and the selected bond distances and angles are provided in Table 1. The coordination sphere of the $Ru_2$ core in **5b** is very similar to that of the parent compound, $Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_3(DMBA\text{-}C_2H)Cl$ (**1**).[13] The Ru−Ru bond distance in **5b** (2.2968(7) Å) is about 0.04 Å shorter than that of **1** (2.3386(6) Å). The averaged bond

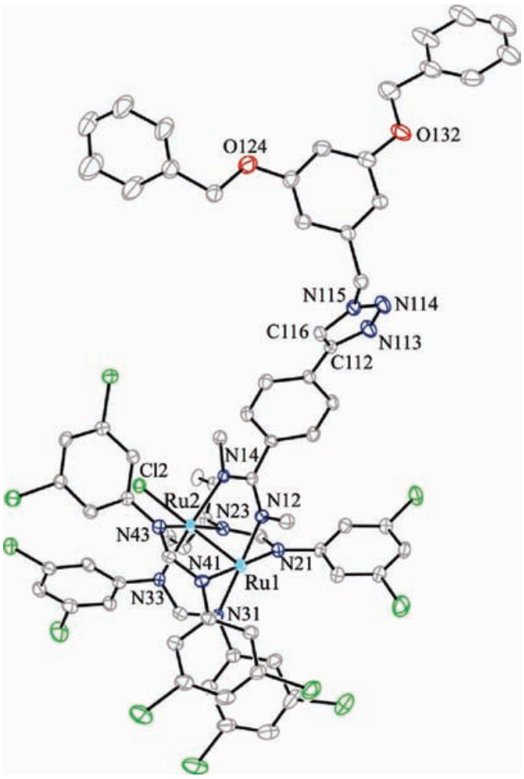


**Figure 1.** ORTEP plot of **5b** at 20% probability level. Hydrogen atoms were omitted for clarity.

### Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 5b

| | | | |
|---|---|---|---|
| Ru1−Ru2 | 2.2968(7) | Ru1−N41 | 2.061(5) |
| Ru2−N14 | 2.056(5) | Ru2−Cl2 | 2.421(2) |
| Ru2−N23 | 2.085(5) | C112−C116 | 1.383(9) |
| Ru2−N33 | 2.116(5) | N115−C116 | 1.351(7) |
| Ru2−N43 | 2.133(5) | N114−N115 | 1.343(7) |
| Ru1−N12 | 2.015(5) | N113−N114 | 1.317(7) |
| Ru1−N21 | 2.050(5) | N113−C112 | 1.352(8) |
| Ru1−N31 | 2.065(5) | | |
| N21−Ru1−Ru2 | 90.41(13) | N14−Ru2−Ru1 | 86.96(13) |
| N31−Ru1−Ru2 | 90.17(14) | N23−Ru2−Ru1 | 87.25(14) |
| N41−Ru1−Ru2 | 90.26(13) | N33−Ru2−Ru1 | 89.19(13) |
| N12−Ru1−Ru2 | 90.40(13) | N43−Ru2−Ru1 | 87.64(13) |
| Ru1−Ru2−Cl3 | 178.82(4) | | |

length of Ru−N (DMBA) is 2.036[5] Å, about 0.05 Å shorter than that of Ru−N (formamidinate), which reflects the strong donor nature of DMBA ligand. The geometry of the 1,2,3-triazole group (C112−C116−N115−N114-N113) in **5b** confirms the regiospecificity of the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction that was noted in prior studies.[10,19] The conformation of the $D_1$ dendron is probably best classified with the descriptor "Ap-Ap-Ap-Ap" according to a recent survey by Stadler.[27]

**Electrochemistry.** Similar to other $Ru_2$ paddlewheel species previously reported from our laboratory,[28] the *click* products reported herein display multiple reversible or quasi-reversible one-electron redox couples, as shown in Figures 2 and 3.

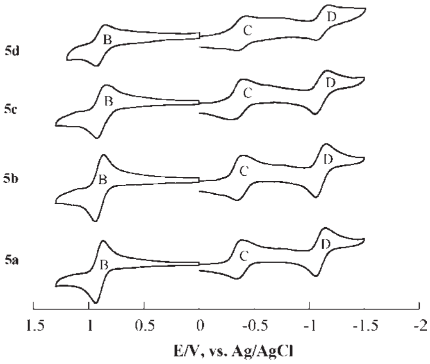


**Figure 2.** Cyclic voltammograms of **5a**−**5d** recorded in a 0.20 M THF solution of $Bu_4NPF_6$ at a scan rate of 0.10 V/s.

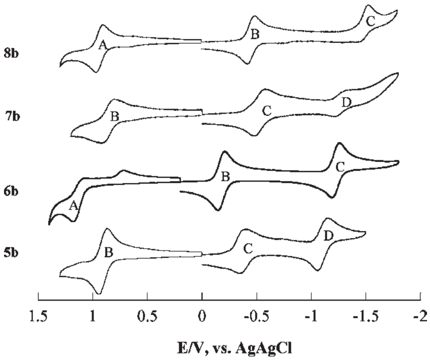


**Figure 3.** Cyclic voltammograms of compounds bearing $\mathbf{D_1}$ dendrons recorded in a 0.20 M THF solution of $Bu_4NPF_6$ at a scan rate of 0.10 V/s.

The $Ru_2$(II,III) compounds **5a**−**5d** (Figure 2), exhibit a reversible oxidation (**B**) and two quasi-reversible reductions (**C** and **D**) with very little variation in the electrode potentials, which are listed in Table 2. All of the observed redox couples are $Ru_2$-based, and their assignments are given in Scheme 2. The electrode potentials ($E_{1/2}$) remain unchanged as the attached dendron expands from $D_0$ (**5a**) to $D_3$ (**5d**), which indicates that the attachment of the various generation dendrons to the periphery has little to no effect in the perturbation of the electronic structure of the $Ru_2$ core. However, it is interesting to note, that while the reversibility of the oxidation couple (**B**) is not affected by the attachment of the various dendrons ($D_0$−$D_3$), both of the reductions (**C** and **D**) become less reversible as the dendron generation increases. This is possibly due to the kinetic hindrance of the reduction processes (slower diffusion) as the dendron expands as noted in prior literature examples.[29] The CV of compound **6b** (a $Ru_2$(III,III) species), displays an irreversible oxidation (**A**), a reversible reduction (**B**), and a quasi-reversible reduction (**C**) (Figure 3). The irreversibility of the couple **A** in compounds **6a**/**6b** is due to the instability of the highly oxidized $Ru_2$(III,IV) species. Compound **8b**, also a $Ru_2$(III,III) species, displays a CV (Figure 3) very different from that of **6b**. It shows one reversible oxidation (**A**), one reversible reduction (**B**), and one irreversible reduction (**C**). The electrode potentials of the redox couples in **8b** were cathodically shifted by at least 120 mV from those of the corresponding couples in **6b**. Clearly, the addition of the second DMBA ligand, a significantly stronger donor than the D(3,5-$Cl_2$Ph)F ligand, results in both easier access to the $Ru_2$(III,IV) couple and more robust Ru−C bonds.

Table 2. Electrochemical Potentials (V, versus Ag/AgCl) of Compounds 5−8

| compound | *E*(**A**) | *E*(**B**) | *E*(**C**) | *E*(**D**) |
|---|---|---|---|---|
| **5a** | NA | 0.897 | −0.353 | −1.108 |
| **5b** | NA | 0.906 | −0.341 | −1.105 |
| **5c** | NA | 0.884 | −0.349 | −1.114 |
| **5d** | NA | 0.897 | −0.383 | −1.108 |
| **6a** | 1.188[a] | −0.173 | −1.226 | NA |
| **6b** | 1.177[a] | −0.187 | −1.234 | NA |
| **7a** | NA | 0.860 | −0.533 | −1.265 |
| **7b** | NA | 0.865 | −0.537 | −1.254 |
| **7c** | NA | 0.895 | −0.516 | −1.367[b] |
| **8a** | 0.954 | −0.431 | −1.481 | NA |
| **8b** | 0.953 | −0.433 | −1.480 | NA |

[a] Irreversible couple, $E_{pa}$ is reported. [b] Irreversible couple, $E_{pc}$ is reported.

Scheme 2. Redox Couple Assignments for Compounds 5−8

$$\mathrm{Ru_2(III,IV)} \underset{\mathbf{A}}{\overset{+\,e^-}{\rightleftharpoons}} \mathrm{Ru_2(III,III)} \underset{\mathbf{B}}{\overset{+\,e^-}{\rightleftharpoons}}$$

$$\mathrm{Ru_2(III,II)} \underset{\mathbf{C}}{\overset{+\,e^-}{\rightleftharpoons}} \mathrm{Ru_2(II,II)} \underset{\mathbf{D}}{\overset{+\,e^-}{\rightleftharpoons}} \mathrm{Ru_2(II,I)}$$

**Photophysical Data.** Both the absorption and fluorescence spectra were recorded for all azidopoly(benzyl ether) dendrons and dendronized $Ru_2$ compounds. Figure 4 displays the electronic absorption spectra of azidopoly(benzyl ether) dendrons ($[D_n]$-$N_3$, $n = 0-3$) in acetonitrile. Each dendron shows an intense UV absorption around 287 nm that increases in intensity as the generation increases from $n = 0$ to $n = 3$, which is consistent with previous literature work.[30] The increase in intensity is not linearly proportional to the increase in the number of phenyl rings as one might expect, which is due to the disruption of conjugation by the ethereal linkages between the phenyl units. The electronic absorption spectra of all hydroxypoly(benzyl ether) dendrons ($[D_n]$−OH, $n = 0-3$) (see Supporting Information, Figure S1) were also measured in acetonitrile solution, which exhibited two intense UV absorptions at 266 and 272 nm with a shoulder at 285 nm. However, at the absorbance maxima of the azido-terminated dendrons (287 nm), the absorbance maxima for the hydroxyl-terminated dendrons is about half of that for the corresponding azido-terminated dendrons, indicating that the azido group has a stronger electronic interaction with the adjacent benzyl group. Also displayed in Figure 4 are the corrected fluorescence spectra of $[D_n]$-$N_3$ ($n = 0-3$) in acetonitrile, where excitation at about 285 nm resulted in fluorescence at about 330 nm. Similar to the absorption spectra, the emission intensity increases as $n$ increases from 0 to 3, while the emission maxima remain constant within the range of a few nanometers.

Shown in Figure 5 are the electronic absorption and fluorescence spectra of three $D_0$-based compounds, **5a**, **6a**, and **7a**, in acetonitrile solution at the same concentration ($6.0 \times 10^{-6}$ M). All three compounds exhibit an intense absorption around 290 nm, which is slightly red-shifted from that of the free dendron (287 nm). The absorption spectrum of the parent compound, **1**, features a UV absorption at 296 nm and a metal-to-ligand charge-transfer (MLCT) absorption at 465 nm.[13] For monosubstituted compound **5a**, the MLCT maximum is similar to that of the parent complex **1.** Similarly for compound **6a** (*bis*-phenylacetylide derivative of **5a**), the MLCT maximum (520 nm) is identical to that observed for $[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}C{\equiv}CSiMe_3)]$-*trans*-$(\sigma\text{-}C{\equiv}CPh)_2$, formally the precursor to **6a.**[13] The absorption spectrum of compound **7a** shows two MCLT absorption maxima at 440 and 500 nm, which is similar to the spectrum of the parent compound **3.**[13] It is clear from these comparisons that the *click* modification has a minimal impact on the MLCT bands. The UV-absorptions are likely the convolution of ligand-to-metal charge transfer (LMCT) (N → Ru) and $\pi-\pi^*$ (dendrons) with the latter being dominant.

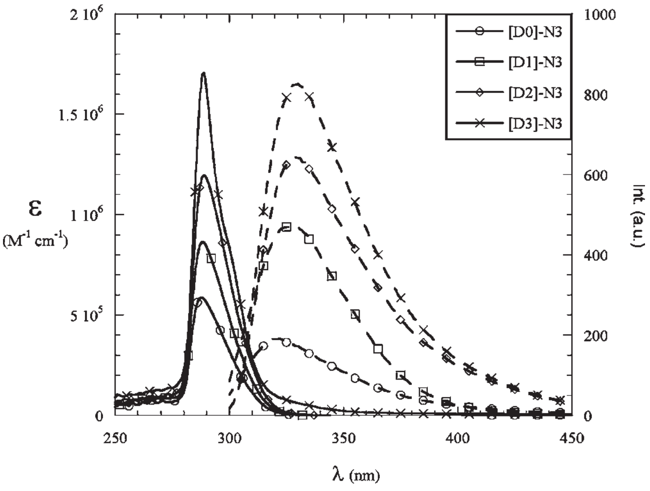


**Figure 4.** Absorption (solid lines) and corrected fluorescence (dashed lines) spectra of a series of $[D_n]$-$N_3$ (where $n = 0-3$) dendrons recorded in $CH_3CN$ solution ($6.0 \times 10^{-6}$ M); $\lambda_{ex} = 285$ nm.

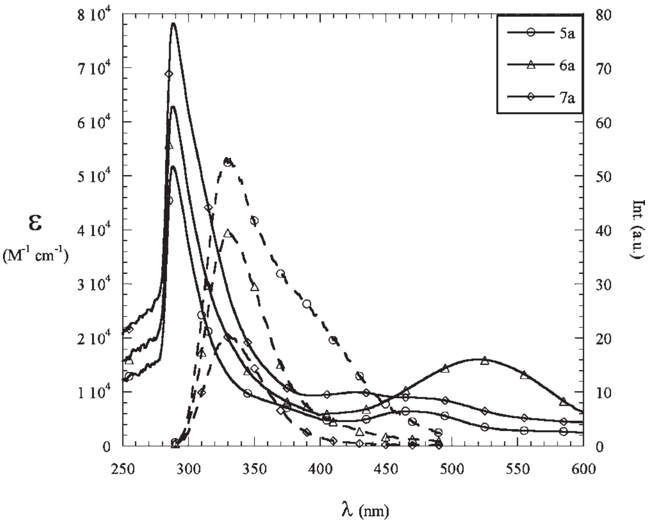


**Figure 5.** Absorption (solid lines) and fluorescence (dashed lines) spectra of a series of $[D_0]$-complexes (**5a**, **6a**, **7a**) recorded in $CH_3CN$ solution ($6.0 \times 10^{-6}$ M); $\lambda_{ex} = 285$ nm.

While the precursor compounds **1**− **4** are nonemissive, the dendritic derivatives are fluorescent. As the examples, shown in Figure 5 are the fluorescence spectra of the $Ru_2$-$[D_0]$ compounds **5a**, **6a**, and **7a** recorded with excitation at 285 nm. Compound **5a** emits at about 330 nm with a shoulder at about 390 nm, the latter

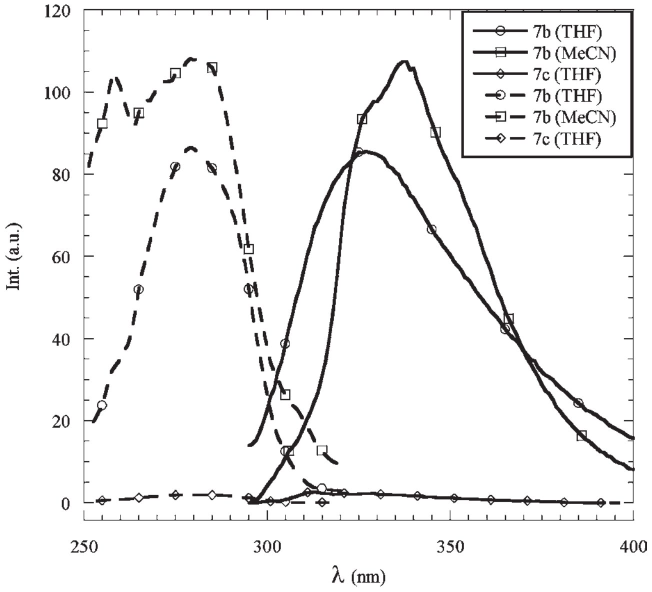


**Figure 6.** Emission (solid lines) and excitation (dashed lines) spectra of disubstituted $[D_1]$-complexes (**7b** and **7c**) recorded in $CH_3CN$ and distilled THF solutions ($6.0 \times 10^{-6}$ M); $\lambda_{ex} = 285$ nm.

of which will be discussed in details below. The emission spectra of compounds **6a** and **7a** on the other hand consist of a single peak around 330 nm, which are less intense than that of compound **5a**. The emission intensities at 330 nm for all three $Ru_2$-based compounds were an order of magnitude lower than that of the corresponding dendron ($[D_0]$-$N_3$), implying that a low-lying nonemissive state localized at the $Ru_2$ core may act as a quencher. Significant reduction in the efficiency of energy transfer from the dendron to the porphyrin core was documented for porphyrins partially substituted by Fréchet dendrons when compared to the fully substituted porphyrins, which was attributed to the emission directly from the dendrons that were less conformationally confined.[31] It is possible that the free rotation of dendrons in our mono- and disubstituted species results in incomplete quenching. To assess the possibility of inefficient energy transfer, the emission and excitation spectra (Figure 6) of **7b** and **7c** were measured in acetonitrile and tetrahydrofuran (THF) solutions of the same concentrations ($6 \times 10^{-6}$ M). While compound **7b** (*cis*-$Ru_2[D_1]_2$) emits in both THF and acetonitrile solutions, compound **7c** (*cis*-$Ru_2[D_2]_2$) exhibited no emission at about 330 nm in THF (insoluble in acetonitrile). This comparison confirms that efficient energy transfer from the dendrons to the $Ru_2$ core is achieved when the dendrons become more conformationally confined, and the observed fluorescence for the $Ru_2$-dendronized compounds in Figure 5 originates from the less conformationally restricted dendrons.

The appearance of a shoulder around 390 nm prompted the further examination of the emission properties of compound **5a** with the excitation varying between 265−315 nm as shown in Figure 7. By gradually increasing the excitation wavelength from 280 to 315 nm (5 nm increments), the peak at 330 nm diminishes while the peak at 390 nm intensifies. Figure 8 shows the excitation spectra resulting from monitoring the emission from 420 nm down to 330 nm, which indicates that the emission maxima at about 390 nm results from irradiation at wavelengths of 300 nm or more. We hypothesize that there are two emissive excited states in the $Ru_2$-dendrons. When the excitation wavelengths are less than 300 nm, the photon energy is sufficient to populate both excited states from which emission can be seen (330 and 390 nm). On the other hand, the photon energy with $\lambda > 300$ nm is sufficient to populate the state that emits at 390 nm, but not the dendron backbone (330 nm). In an attempt to ascertain the location of the second emissive state, the emission and excitation of the model dendron, $C_6H_5-C_2N_3H_2-CH_2$-$(C_6H_5)$ (*click* product of phenylacetylene and $[D_0]$-$N_3$), were measured in acetonitrile solutions at $6 \times 10^{-6}$ M (see Supporting Information, Figure S2). Both the excitation and the emission spectrum closely resembled those of the free dendrons (Figure 4) and there was an appearance of a shoulder at about 395 nm (Int. (a.u.) = 10) when moving the excitation wavelength to lower energy (>370 nm). These results raised the possibility of the newly formed triazole ring as the source of emission at 390 nm.

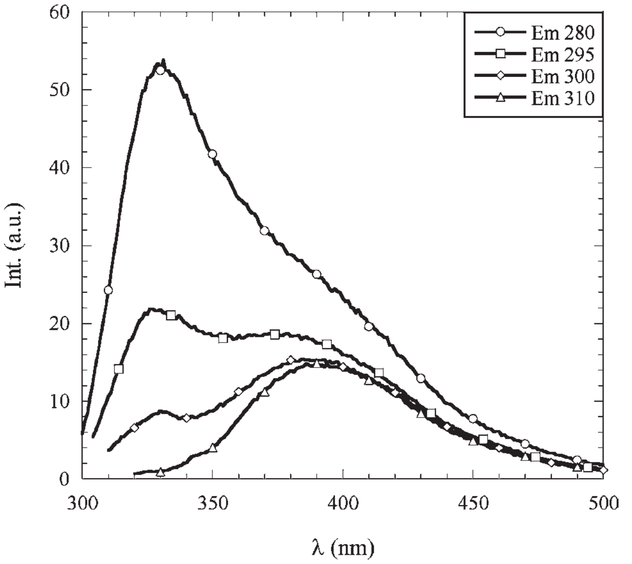


**Figure 7.** Fluorescence emission spectra of compound **5a** recorded in $CH_3CN$ solution ($6.0 \times 10^{-6}$ M).

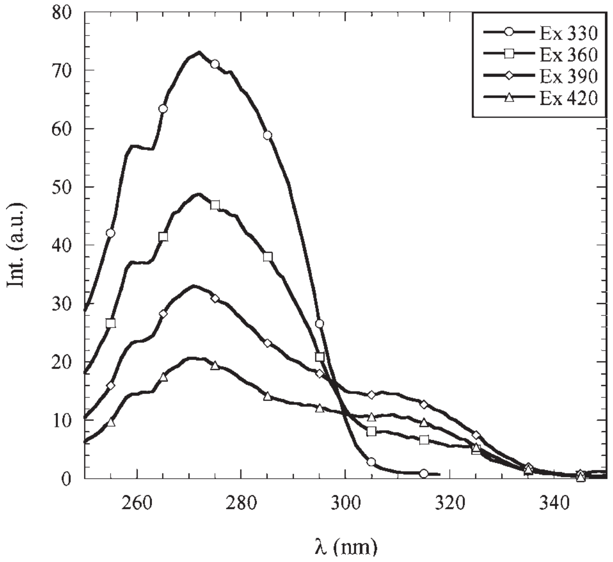


**Figure 8.** Fluorescence excitation spectra of compound **5a** recorded in $CH_3CN$ solution ($6.0 \times 10^{-6}$ M).

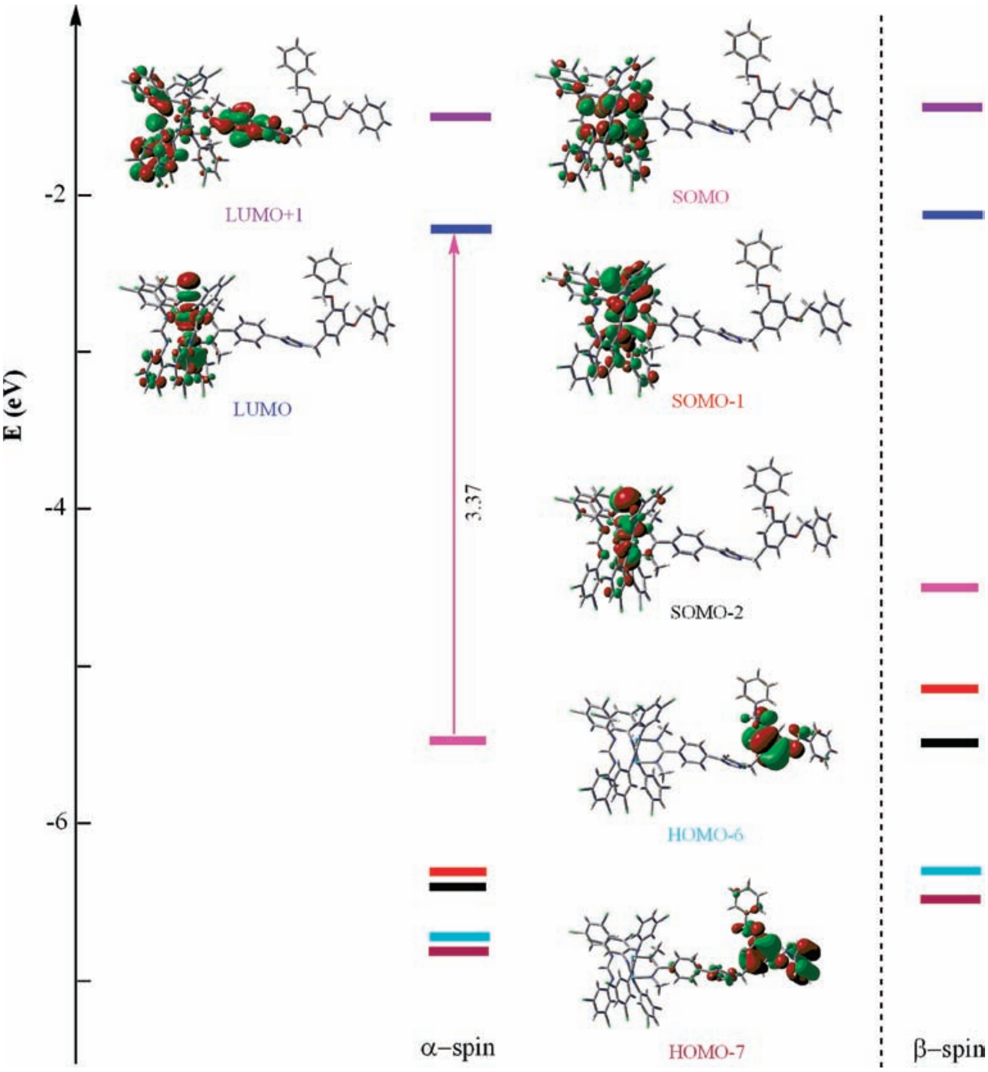


**Figure 9.** MO diagram of model compound **5′** based on spin-unrestricted DFT calculations; energy levels for both spins are provided, and only the $\alpha$ spin Kohn−Sham orbitals are shown.

To better understand both the electronic structure and spectral characteristics of dendron-modified diruthenium species, DFT calculations at the B3LYP/LanL2DZ level (Gaussian 03 suite)[32] were performed on the model compound **5′**. The geometry of compound **5′** was optimized from the crystal structure of **5b** without truncation, and the optimized bond lengths and angles related to the $Ru_2$ coordination sphere (Supporting Information, Table S1) agree well with those from the crystal structure. Because of the paramagnetic nature of $Ru_2$(II,III) species, the spin-unrestricted DFT calculations for **5′** were performed and converged to a configuration with the singly occupied molecular orbital (SOMO), SOMO−1, and SOMO−2 being energetically close and singly occupied. As shown in Figure 9, the SOMO is dominated by the $\delta^*$(Ru−Ru) orbital, while the SOMO−1 and SOMO-2 are nearly degenerate and predominantly $\pi^*$(Ru−Ru) in nature. Hence, the spin-unrestricted DFT produced the $\pi^{*2}\delta^{*1}$ configuration that has been well established for $Ru_2$(II,III) species based on the temperature dependence of magnetic susceptibility.[33] The LUMO is dominated by $\sigma^*$(Ru−Ru) and also contains significant contribution of $\sigma^*$(Ru−Cl).

Among the ligand dominated empty MOs, the DMBA phenyl ring typically exhibits localized electronic characteristics due to its orthogonal orientation to the N−C−N bridge, resulting in weak electronic delocalization between the dendron and the $Ru_2$ core. The LUMO +1 contains significant contribution from the antibonding combination of the DMBA phenyl $\pi$ orbital and triazole $\pi$ orbital, implying a possible role of the phenyl-triazole linkage in mediating energy transfer from the dendron periphery to the metal core (the Dexter type). Also noteworthy are the low lying HOMO-6 and HOMO-7, both with a dominant character of the dendron $\pi$-orbitals, which are likely responsible for the absorption of UV photons by the dendron ligands (photonic antennae). Time-dependent DFT (TD-DFT) calculations of model **5′** would be ideal in providing quantitative assignment of the observed absorption/emission characteristics. These calculations, however, exceed the computational resources currently available to us.

## ■ CONCLUSION

$Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(DMBA\text{-}I)_mCl$ (DMBA-I is *N,N′*-dimethyl-4-iodobenzamidinate) type compounds were synthesized and prepared according to literature procedures. These $Ru_2$ complexes were further derivatized on their periphery using the Sonogashira cross-coupling reaction and the Cu(I)-catalyzed 1, 3-dipolar cycloaddition (*click* reaction) to yield terminal alkynes and dendronized $Ru_2$ complexes, respectively. These results are important in illustrating that the peripheral ligand environment surrounding the $Ru_2$ core can be altered with little disruption of the electronic properties of the $Ru_2$ bimetallic center.[11] Most of dendritic inorganic compounds of a mononuclear focal point were prepared from ligands that were already dendronized.[34] However, our group has shown the possibility of synthesizing inorganic compounds through peripheral ligand modification. With these results, an avenue for inorganic supramolecular chemistry is opened. The next step is to explore new $Ru_2$ paddlewheel complexes with different bidentate auxiliary ligands in hope that these complexes can be combined with more conjugated dendrons (photonic antennae) for the harvesting of solar energy. The more we learn about the photochemistry and photophysics of $Ru_2$ paddlewheel complexes by altering the bidentate ligands and the conjugated dendrons, the closer we are at realizing novel organometallic photovoltaic materials.

## ■ EXPERIMENTAL SECTION

**General Information.** Dendrons $D_n$-$N_3$ ($n$ = 0−3) were synthesized according to the literature procedure.[35] $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)X$ (X = Cl, **1** and X = $(C_2Ph)_2$, **2**) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2X$ (X = Cl, **3** and X = $(C_2Ph)_2$, **4**) type complexes were prepared as previously described.[13] $CuSO_4 \cdot 5H_2O$ and sodium ascorbate were purchased from ACROS. Phenylacetylene was purchased from GFS, and *n*-BuLi (2.5 M in hexanes) was purchased from Sigma-Aldrich. $^1H$ NMR spectra were obtained using a Varian Mercury 300 NMR and a Bruker400 NMR spectrometer, with chemical shifts ($\delta$) referenced to the residual $CHCl_3$, respectively. Magnetic susceptibility was measured at 294 K with a Johnson Matthey Mark-I magnetic susceptibility balance. UV−vis spectra were recorded at 294 K in THF (**7c**) or $CH_3CN$ solutions in 1 cm quartz cuvettes on a JASCO V-670 spectrophotometer. Emission spectra were recorded on a Varian Cary Eclipse fluorimeter in $CH_3CN$ (THF for compound **7c**) solution. All nano-ESI (nESI) mass spectral data were performed on a QqQ tandem mass spectrometer in $CH_2Cl_2$ or THF solutions (QTRAP2000, Applied Biosystems/MDS Sciex, Concord, ON, Canada). All HR-nESI-MS data was performed on a modified QqTOF tandem mass spectrometer in $CH_2Cl_2$ (QSTAR XL; mass resolving power ∼8000 amu; mass accuracy ∼20 ppm; Applied Biosystems/MDS Sciex, Concord, ON, Canada). Masses were calculated by isotopic distribution utilizing Analyst 1.4 software (Applied Biosystems/MDS Sciex, Concord, ON, Canada). Elemental analysis was performed by Atlantic Microlab, Norcross, GA. Cyclic voltammograms were recorded in a 0.2 M $(n\text{-}Bu)_4NPF_6$ solution (THF, $N_2$-degassed) on a CHI620A voltammetric analyzer with a glassy-carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. The concentration of $Ru_2$-species is always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.570 V (vs Ag/AgCl) at the noted experimental conditions.

**General Procedure for *click* Reactions between Azidopoly(benzyl ether) Dendrons ($[D_0]$-$N_3$ to $[D_3]$-$N_3$) and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)X$ (Where X = Cl or $(C_2Ph)_2$).** $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)X$ (1 equiv) and the appropriate dendron ($[D_n]$-$N_3$, 1.2 equiv) were dissolved in THF (ca. 10 mL of THF per 100 mg of $Ru_2$ complex). To this solution, an equivalent volume of $H_2O$ to THF was added while stirring vigorously at room temperature. Sodium ascorbate (10 mol %) and $CuSO_4 \cdot 5H_2O$ (5 mol %) were added sequentially to the reaction mixture from freshly prepared aqueous solutions (1.0 M). Upon the addition of sodium ascorbate, the reaction mixture turned red for a few seconds and then a dark precipitate formed. Reactions that had reached completion, usually overnight, had become a suspension mixture. To the reaction mixture was then added 100 mL of $H_2O$, and followed by extraction with $CH_2Cl_2$ (3×). Organic phase was collected and dried over $MgSO_4$. After removal of the solvent, the residue was purified from flash chromatography followed by recrystallization from THF/hexanes.

**General Procedure for *click* Reactions between Azidopoly(benzyl ether) Dendrons ($[D_0]$-$N_3$ to $[D_2]$-$N_3$) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2X$ (Where X = Cl or $(C_2Ph)_2$).** *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2X$ (1 equiv) and the appropriate dendron ($[D_n]$-$N_3$, 2.2 equiv) were dissolved in THF (ca. 20 mL THF per 100 mg of $Ru_2$ complex). To this solution, a $H_2O$-THF mixed solvent (v/v, 1:1) was added while stirring vigorously at room temperature. Sodium ascorbate (20 mol %) and $CuSO_4 \cdot 5H_2O$ (10 mol %) were added sequentially to the reaction mixture in the form of freshly prepared aqueous solutions (1.0 M). Upon the addition of $CuSO_4 \cdot 5H_2O$, a dark precipitate formed. The reaction was monitored by TLC and usually went to completion overnight. To the reaction mixture was then added 100 mL of $H_2O$, and followed by extraction with $CH_2Cl_2$ (3×). Organic phase was collected and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (EtOAc/hexanes = 1:2) and recrystallization from THF/hexanes.

**Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_0)Cl$ (5a).** This compound was prepared from 0.060 g (0.043 mmol) of compound **1** and was purified via flash chromatography eluting with 1:10 THF/hexanes to 1:2 THF/hexanes. Yield: 0.015 g (0.010 mmol), 23%. HR-nESI-MS: $m/e$ 1506.706, corresponding to $[M - Cl + H]^+$ (calc. 1506.685). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 288 (51,800), 468 (6,400). $\chi_{mol}$(corrected) = $6.26 \times 10^{-3}$ emu, $\mu_{eff}$ = 3.86 $\mu_B$ Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.897, 0.082, 0.914; **C**, −0.353, 0.053, 0.894; **D**, −1.108, 0.118, 0.667.

**Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_1)Cl$ (5b).** This compound was prepared from 0.30 g (0.213 mmol) of compound **1** and was purified via flash chromatography eluting with 1:10 THF/hexanes to 1:2 THF/hexanes. Yield: 0.34 g (0.19 mmol), 91%. nESI-MS: $m/e$ 1719, corresponding to $[M - Cl + H]^+$. UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 287 (63,500), 468 (7,000). $\chi_{mol}$(corrected) = $6.27 \times 10^{-3}$ emu, $\mu_{eff}$ = 3.86 $\mu_B$ Anal. for $C_{71}H_{51}Cl_{13}N_{11}O_2Ru_2 \cdot THF$, Found (calcd.): C, 49.43 (49.35); H, 3.01 (3.26); N, 8.54 (8.44). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.906, 0.079, 0.946; **C**, −0.341, 0.057, 0.861; **D**, −1.105, 0.095, 0.873.

**Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_2)Cl$ (5c).** This compound was prepared from 0.06 g (0.043 mmol) of compound **1** and was purified by recrystallization from $CH_2Cl_2$/hexanes (1:9). Yield: 0.07 g (0.033 mmol), 77%. nESI-MS: $m/e$ 2143, corresponding to $[M - Cl + H]^+$. UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 288 (82,000), 466 (6900). $\chi_{mol}$(corrected) = $6.26 \times 10^{-3}$ emu, $\mu_{eff}$ = 3.86 $\mu_B$ Anal. for $C_{99}H_{75}Cl_{13}N_{11}O_6Ru_2 \cdot 2C_6H_{14}$, Found(calcd.): C, 56.42 (56.73); H, 4.15 (4.42); N, 6.48 (6.56). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.884, 0.080, 0.883; **C**, −0.349, 0.119, 0.847; **D**, −1.114, 0.119, 0.919.

**Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_3)Cl$ (5d).** This compound was prepared from 0.10 g (0.071 mmol) of compound **1** and was purified by recrystallization from THF/hexanes (1:9). Yield: 0.11 g (0.036 mmol), 51%. nESI-MS: $m/e$ 2991, corresponding to $[M - Cl + H]^+$. UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 289 (109,000), 466 (6,700). $\chi_{mol}$(corrected) = $6.28 \times 10^{-3}$ emu, $\mu_{eff}$ = 3.64 $\mu_B$ Anal. for $C_{155}H_{123}Cl_{13}N_{11}O_{14}Ru_2 \cdot 3C_6H_{14}$, Found(calcd.): C, 63.60 (63.25); H, 4.71 (5.06); N, 4.26 (4.26). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.897, 0.082, 0.814; **C**, −0.383, 0.083, 0.794; **D**, −1.108, 0.118, 0.667.

**Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_0)(C_2Ph)_2$ (6a).** This compound was prepared from 0.100 g (0.071 mmol) of compound **2** and was purified by column chromatography (1:5 THF/hexanes) followed by recrystallization from THF/hexanes (1:9). Yield: 0.0261 g (0.017 mmol), 24%. $^1$H NMR: 8.23 (s, 3H, NC*H*N), 8.14 (s, 1H, NC*H*N), 7.99−7.97 (d, 2H, Ar*H*), 7.31−6.50 (m, 36H, Ar*H*), 5.55 (s, 2H, C*H*$_2$), 3.63 (s, 6H, NC*H*$_3$). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 270 (76,600), 515 (21,300). HR-nESI-MS: *m/e* 1628.721, corresponding to $[M - Ph - H]^-$ (calc. 1628.7173). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: $E_{pa}$(**A**), 1.188; **B**, −0.173, 0.033, 1.000; **C**, −1.226, 0.038, 0.892.

**Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}D_1)(C_2Ph)_2$ (6b).** To a 40 mL THF solution of **5b** 0.30 g, (0.17 mmol), 5 equiv of PhCCLi was added. The color of the reaction mixture changed to red immediately. After stirring under $N_2$ for 5 min, the reaction mixture was bubbled with $O_2$. The purification of the title product was performed by chromatography (1:5 THF/hexanes). Yield: 0.17 g (0.089 mmol), 52%. nESI-MS: *m/e* 1919, corresponding to $[M - H]^-$. $^1$H NMR: 8.25 (s, 3H, NC*H*N), 8.15 (s, 1H, NC*H*N), 8.02−7.97 (d, 2H, Ar*H*), 7.34−6.48 (m, 44H, Ar*H*), 5.54 (s, 2H, C*H*$_2$), 5.01 (s, 4H, C*H*$_2$), 3.67 (s, 6H, NC*H*$_3$). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 269 (90,400), 518 (21,200). Anal. for $C_{87}H_{61}Cl_{12}N_{11}O_2Ru_2$, Found(calcd.): C, 54.55 (54.31); H, 3.44 (3.41); N, 7.55 (8.01). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: $E_{pa}$(**A**), 1.177; **B**, −0.187, 0.064, 0.975; **C**, −1.234, 0.071, 0.888.

**Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_0)_2Cl$ (7a).** This compound was prepared from 0.270 g (0.217 mmol) of compound **3** and 2.2 equiv of $[D_0]$-$N_3$. The purification of the title product was performed by column chromatography eluting with 1:4 THF/hexanes to 1:1:0.5 THF/hexanes/acetone, followed by recrystallization from $CH_2Cl_2$/hexanes (1:7). Yield: 0.2764 g (0.181 mmol), 84%. HR-nESI-MS: *m/e* 1488.954, corresponding to $[M - Cl + H]^+$ (calc. 1488.943). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 286 (79,100), 427 (9,940), 482 (8,790). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.860, 0.059, 0.873; **C**, −0.533, 0.051, 0.969; **D**, −1.265, 0.054, 0.973.

**Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_1)_2Cl$ (7b).** This compound was prepared from 0.065 g (0.045 mmol) of compound **3** and 2.2 equiv of $[D_1]$-$N_3$. The purification of the title product was performed by column chromatography eluting with 1:4 THF/hexanes to 1:2:0.5 THF/hexanes/acetone, followed by recrystallization from $CH_2Cl_2$/hexanes (1:7). Yield: 0.055 g (0.033 mmol), 51%. HR-nESI-MS: *m/e* 1902.469, corresponding to $[M - Cl + H]^+$ (calc. 1902.439). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 266 (124,000), 272 (122,000), 286 sh (93,500), 427 (7,970), 482 (6,870), 650 (2,840). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.865, 0.036, 0.719; **C**, −0.537, 0.056, 0.932; **D**, −1.254, 0.055, 0.833.

**Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_2)_2Cl$ (7c).** Compound **3** (Scheme 1) (0.150 g, 0.120 mmol) and 2.2 equiv of $[D_2]$-$N_3$ were dissolved in 10 mL of THF. To this solution, 10 mL of $H_2O$ was added. Sodium ascorbate (20 mol %) and $CuSO_4 \cdot 5H_2O$ (10 mol %) were added sequentially to the reaction mixture while stirring vigorously at room temperature. The mixture was allowed to stir overnight in air, but the title product was not achieved. The monosubstituted, *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}C_2H)(DMBA\text{-}D_2)Cl$, complex was isolated and verified via nESI-MS (*m/e* 1971, corresponding to $[M - Cl + H]^+$). The title compound was achieved by reacting the purified monosubstituted complex with 2.2 equiv of $[D_2]$-$N_3$ under the same conditions initially set forth. The reaction mixture was poured into 50 mL of $H_2O$ followed by extraction with $CH_2Cl_2$. The organic phase was collected and dried over $MgSO_4$ overnight. The purification of the title product was achieved via recrystallization from THF/hexanes followed by flash chromatography (1:1:0.5 $CH_2Cl_2$/hexanes/acetone). Yield: 0.096 g (0.068 mmol), 57%. HR-nESI-MS for **7c**·$H_2O$: *m/e* 1402.777, corresponding to $[M - Cl + 2H]^{2+}$ (calc. 1402.954) UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)in THF): 266 (151,000), 272 (135,000), 287 sh (93,800), 426 (8,113), 480 (6,873), 652 (3,306). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **B**, 0.895, 0.049, 0.674; **C**, −0.516, 0.054, 0.948; **D**, $E_{pc}$ = −1.367.

**Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_0)_2(C_2Ph)_2$ (8a).** This compound was prepared from 0.110 g (0.077 mmol) of compound **4** and 2.2 equiv of $[D_0]$-$N_3$. The purification of the title product was performed by column chromatography eluting with 1:4 EtOAc/hexanes to 1:2 EtOAc/hexanes, followed by recrystallization from $CH_2Cl_2$/hexanes (1:7). Yield: 0.055 g (0.033 mmol), 46%. nESI-MS: *m/e* 1600, corresponding to $[M - Ph - H]^-$. $^1$H NMR: 8.10 (s, 2H, NC*H*N), 8.03−7.94 (d, 4H, Ar*H*), 7.54−6.44 (m, 38H, Ar*H*), 5.52 (s, 4H, ArC*H*$_2$), 3.34 (s, 12H, NC*H*$_3$). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 274 (120,000), 515 (19,000). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: (**A**), 0.954, 0.049, 0.939; **B**, −0.431, 0.049, 1.000; **C**, −1.481, 0.066, 0.465.

**Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}D_1)_2(C_2Ph)_2$ (8b).** This compound was prepared from 0.130 g (0.092 mmol) of compound **4** and 2.2 equiv of $[D_1]$-$N_3$. The purification of the title product was performed by column chromatography (1:2 EtOAc/hexanes). Yield: 0.11 g (0.052 mmol), 57%. ESI-MS: *m/e* 2108, corresponding to $[M - H]^-$. $^1$H NMR: 8.11 (s, 2H, NC*H*N), 8.03−7.95 (d, 4H, Ar*H*), 7.54−6.48 (m, 54H, Ar*H*), 5.54 (s, 4H, ArC*H*$_2$), 5.03 (s, 8H, ArC*H*$_2$O), 3.37 (s, 12H, NC*H*$_3$). Anal. for $C_{106}H_{88}Cl_8N_{14}O_4Ru_2 \cdot C_6H_{14}$, Found(calcd.): C, 61.38 (61.32); H, 4.53 (4.69); N, 8.43 (8.94). UV−vis, $\lambda_{max}$(nm, $\varepsilon$ ($M^{-1}$ $cm^{-1}$)): 276 (134,000), 516 (18,900). Cyclic voltammogram [$E_{1/2}$/V, $\Delta E_p$/V, $i_{backward}/i_{forward}$]: **A**, 0.953, 0.063, 0.883; **B**, −0.433, 0.063, 0.862; **C**, −1.480, 0.075, 0.909.

**X-ray Data Collection, Processing, and Structure Analysis and Refinement for Crystal 5b.** Single crystals of compound **5b** were grown via slow evaporation of a THF/hexanes solution. A dark plate having approximate dimensions of 0.38 × 0.33 × 0.09 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) on a Nonius KappaCCD equipped with a graphite crystal, incident beam monochromator. Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 29746 reflections in the range $2 < \theta < 24°$. The hexagonal cell parameters and calculated volume are as follows: $a$ = 29.1361(13), $c$ = 55.364(3) Å, $V$ = 40702(3) Å$^3$. For $Z$ = 18 and F.W. = 1753.30, the calculated density is 1.29 g/cm$^3$. The space group was determined by the program XPREP to be $R\bar{3}$. The data were collected at a temperature of 150(1) K. The structure was solved by direct methods using SIR2004 and refined using the SHELX-97.[36]

**Computational Methods.** The full geometry optimization of model compound **5′** was based on the crystal structure of **5b** using the DFT method, which was based on the hybrid B3LYP density functional model[37] within the Gaussian 03 suite programs.[32] In the calculations, quasi-relativistic pseudopotentials of the Ru 16 valence electrons are employed and the LanL2DZ basis sets associated with the pseudopotential were adopted.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Additional spectra and DFT details of model compound **5′**, and X-ray crystallographic details (CIF) of **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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