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Electrochemical and Spectroscopic Behaviors of a Novel Ruthenium(II) Complex with a Six-Membered Chelate Structure

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Supporting Information

ABSTRACT: A novel polypyridyl ruthenium(II) complex with a sixmembered chelate ring ($[Ru(dmb)_2(8pyq)]^{2+}$) was designed and synthesized. The oxidation potential was shifted to the negative potential direction, and relatively intense metal-to-ligand charge transfer absorption in the longerwavelength region was observed for $[Ru(dmb)_2(8pyq)]^{2+}$ compared with the reference complexes without any six-membered chelate rings. The electrochemical and spectroscopic properties of [Ru(dmb)₂(8pyq)]²⁺ were discussed in terms of the chelate structure and coordination geometry with utilization of theoretical calculations.



INTRODUCTION

The metal-to-ligand charge transfer (MLCT) excited states of polypyridyl complexes of ruthenium(II), rhenium(I), iridium-(III), and so forth are characteristic for metal complexes and one of the most extensively utilized excited states. As represented by $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) and its derivatives,¹ most of the MLCT-type metal complexes exhibit intense visible-light absorption and, furthermore, $d\pi^{6}$ -type transition metal complexes often show phosphorescence from their long-lived triplet MLCT (³MLCT) excited states. In these complexes, nominally spin-forbidden processes are partially allowed owing to the spin-orbit coupling arising from the heavy atom effect of the metal center. Owing to such intense visible-light absorption/emission and long-lived excited state, a class of the complexes has been utilized in a variety of photochemical applications: e.g., photosensitizers in solarenergy conversion systems such as dye-sensitized solar cells^{2-5} and artificial photosynthesis⁶⁻¹¹ or triplet emitters in organic light-emitting diodes.^{12–16} Because the excited-state properties (e.g., light absorption, emission, photoinduced reactions) of the complexes are affected largely by the electronic structures of both metal center and ligand structure, various MLCT-type complexes have been hitherto developed.

The MLCT transition in an octahedral d⁶-metal complex corresponds to an electronic transition from the $t_{2\sigma}$ orbital of the metal center to the π^* orbital of a ligand(s). On the basis of the classical crystal-field (or ligand-field) theory, intrinsically degenerated five d orbitals of the metal center split to three occupied t_{2g} and two unoccupied e_g orbitals in energy, and the extent of the energy splitting is predominated by the octahedral coordination sphere around the metal. However, the MLCT-type complexes with bidentate or tridentate ligand(s) (e.g., $[Ru(bpy)_3]^{2+}$) often possess five-membered chelate ring(s) and, in many cases, the steric displacements of the coordinating atoms deviate from the ideal octahedral

geometry. Therefore, we expected that an introduction of a sixmembered chelate structure in a complex can change the coordination geometry around the metal center and that it should be an important factor to control the electronic structures of the complex in the ground and excited states. Although acetylacetonate (acac) and its derivatives are famous examples to give six-membered chelate rings,^{17,18} they rarely act as the acceptor ligand for the MLCT transition. In this study, a novel ruthenium(II) complex with a six-membered chelate ring $([Ru(dmb)_2(8pyq)]^{2+}$ where dmb = 4,4'dimethyl-2,2'-bipyridine and 8pyq = 8-(pyridin-2-yl)quinoline) was designed and synthesized.



Owing to the low-energy π^* orbital of 8pyq and the electrondonating nature of the methyl groups in the dmb ligands, 8pyq acts as an acceptor ligand in the lowest-energy MLCT excited state of the complex. The effects of the six-membered chelate

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Figure 1. Optimized geometries of $[Ru(dmb)_2(8pyq)]^{2+}$ (a) and $[Ru(dmb)_2(bpy)]^{2+}$ (b) with an overlaid comparison (c) of the RuN₆ moieties for $[Ru(dmb)_2(8pyq)]^{2+}$ (purple) and $[Ru(dmb)_2(bpy)]^{2+}$ (green). Hydrogen atoms are omitted for clarity.

structure given by a coordination of 8pyq to the ruthenium(II) center on the electrochemical/spectroscopic properties of the complex were evaluated and compared with those of the reference complexes without any six-membered chelates.

EXPERIMENTAL SECTION

Chemicals. $[\operatorname{Ru}(\operatorname{bpy})_3](\operatorname{PF}_6)_2$ is the same sample which has been used in the earlier literature.^{19–21} Tetra-*n*-butylammonium hexa-fluorophosphate (TBAPF₆, Wako Pure Chemical Industries) was purified by repeated recrystallizations from ethanol. Ferrocene (Wako Pure Chemical Industries) was used as supplied. Anhydrous or spectroscopic-grade CH₃CN (Wako Pure Chemical Industries) was used without further purification for the electrochemical or spectroscopic measurements, respectively.

Electrochemical Measurements. Cyclic voltammetry of the complexes in CH₃CN at 298 K was performed by using a BAS ALS-1202A electrochemical analyzer with a three-electrode system using glassy-carbon working, Pt auxiliary, and Ag/AgNO₃ reference electrodes (\sim 0.01 M in CH₃CN containing \sim 0.1-M TBAPF₆) supplied by BAS Inc. The sample solutions containing a complex (\sim 1.0 mM) and TBAPF₆ as a supporting electrolyte (\sim 0.1 M) in the absence or presence of ferrocene were deaerated by purging an argon gas stream over 20 min prior to measurements. The potential sweep rate was 100 mV/s.

Spectroscopic Measurements. The absorption spectra of the complexes were measured by using a Hitachi U-3500 spectrophotometer. The emission spectra were obtained by using a Hitachi F-4500 spectrofluorometer (excitation wavelength: 450 nm), and emission intensity at each wavelength was corrected for system spectral response so that the vertical axis of a spectrum corresponds to the photon number at each wavelength. The emission quantum yields (Φ_{em}) were determined relative to that of $[Ru(bpy)_3](PF_6)_2$ ($\Phi_{em,std} = 0.095$ in CH₃CN^{22,23}) on the basis of eq 1.

$$\Phi_{\rm em} = \frac{\int I_{\rm sample}(\tilde{\nu}) d\tilde{\nu}/A_{\rm sample}}{\int I_{\rm std}(\tilde{\nu}) d\tilde{\nu}/A_{\rm std}} \times \Phi_{\rm em, std}$$
(1)

In eq 1, the subscripts "sample" and "std" represent a sample complex and standard (i.e., $[\operatorname{Ru}(\operatorname{bpy})_3](\operatorname{PF}_6)_2$), respectively, and *A* is the absorbance at an excitation wavelength. $I(\tilde{\nu})$ is emission intensity (photon scale) at a wavenumber $\tilde{\nu}$, which was corrected by the equation $I(\tilde{\nu}) = I(\lambda) \times \lambda^{2.24,25}$ It should be noted that, in eq 1, a correction for the difference in the refractive indices between the sample and standard solutions was omitted because the same solvent was used for all the solutions and solute concentrations were quite low (<5 × 10⁻⁶ M). For the emission measurements, the absorbance of a sample solution was set <0.05 at 450 nm to avoid the self-absorption and inner filter effect, and sample solutions were deaerated by purging with an argon gas stream for over 30 min.

Theoretical Calculations. Theoretical calculations for the complexes were conducted with Gaussian 16W software (Revision A.03).²⁶ The ground-state geometries of the complexes were optimized by using density functional theory (DFT) using the restricted B3LYP functional 27,28 with LanL2DZ $^{29-31}$ and 6-31G- $(d,p)^{32}$ basis sets for ruthenium and all other atoms, respectively. Frequency calculations for the optimized geometries by identical methodologies did not give any negative frequencies, irrespective of the complex. Time-dependent DFT (TD-DFT) calculations were then performed to estimate the energies and oscillator strength of the 50 lowest-energy singlet and 3 triplet absorption transitions by employing the same functional and basis sets with geometry optimizations. Natural transition orbitals were plotted using Gauss-View 6.33 All the calculations were carried out as in acetonitrile (dielectric constant = 35.688, square of refractive index = 1.806874) by using a polarizable continuum model using the integral equation formalism variant (IEFPCM).34

RESULTS AND DISCUSSION

Synthesis and Characterization. $[\operatorname{Ru}(\operatorname{dmb})_2(\operatorname{8pyq})]^{2+}$ was successfully synthesized via a typical synthetic route shown in Scheme S1. 8pyq was synthesized according to the literature³⁵ and then introduced into a metal complex. A PF₆⁻ ion was selected as the counterion of the complex due to high solubility of the PF₆⁻ salt of polypyridyl ruthenium(II) complex in polar organic solvents. $[\operatorname{Ru}(\operatorname{dmb})_2(\operatorname{8pyq})](\operatorname{PF}_6)_2$ was adequately identified by the ¹H NMR measurements, high-resolution mass spectrometry (HRMS), and elemental analysis. Although the complex possesses Δ - and Λ -isomers around the ruthenium(II) center, they have not been separated because it can be expected that they do not affect the electrochemical and spectroscopic properties of the complex conducted in this study.

Because any crystals suitable for crystallographic analysis were, unfortunately, not obtained, the steric structure of $[Ru(dmb)_2(8pyq)]^{2+}$ was discussed on the basis of the optimized geometry by the DFT calculations. Figure 1 shows optimized geometries of $[Ru(dmb)_2(8pyq)]^{2+}$ and $[Ru-(dmb)_2(bpy)]^{2+}$. Selected N–Ru–N angles and Ru–N bond lengths of the complexes are also summarized in Table 1 (for full data of nuclear coordinates, see Tables S1 and S2). Significant influences of an introduction of the six-membered chelate structure on the coordinates with the ruthenium(II) center

Table 1. Selected Angles and Bond Lengths for Optimized Geometries of $[Ru(dmb)_2(8pyq)]^{2+}$ and $[Ru(dmb)_2(bpy)]^{2+}$

	angle/length			
atoms	$[Ru(dmb)_2(8pyq)]^{2+}$	$[Ru(dmb)_2(bpy)]^{2+}$		
N1-Ru-N2	87.54°	77.80°		
N3-Ru-N4	77.52°	77.60°		
N5-Ru-N6	77.25°	77.58°		
N1-Ru-N6	174.27°	172.91°		
N2-Ru-N3	173.40°	172.85°		
N4-Ru-N5	171.96°	172.53°		
Ru–N1	2.156 Å	2.110 Å		
Ru–N2	2.133 Å	2.110 Å		
Ru–N3	2.112 Å	2.112 Å		
Ru–N4	2.115 Å	2.112 Å		
Ru-N5	2.132 Å	2.112 Å		
Ru–N6	2.109 Å	2.112 Å		

almost orthogonally with a chelating N-Ru-N angle of 87.54°, whereas corresponding angles by a bpy-type ligand (i.e., bpy or dmb) are $\sim 78^{\circ}$. Furthermore, the 8pyq ligand enlarges the N-Ru-N angle for two nitrogen atoms at the trans position to be $\sim 174^{\circ}$. These results suggest that a coordination geometry of $[Ru(dmb)_2(8pyq)]^{2+}$ is closer to the ideal octahedral structure than those of the typical polypyridyl ruthenium(II) complexes such as $[Ru(dmb)_2(bpy)]^{2+}$. On the other hand, the Ru–N bond lengths for the 8pyq ligand (2.156 and 2.133 Å for Ru-N1 (quinoline) and Ru-N2 (pyridine), respectively) significantly increase in comparison with those in $[Ru(dmb)_{2}(bpy)]^{2+}$ (2.110–2.112 Å). Furthermore, it must be noted that the 8pyq ligand itself in the optimized [Ru- $(dmb)_2(8pyq)$ ²⁺ geometry is largely distorted: the dihedral angle between pyridine and quinoline moieties is 37°, and the quinoline ring resides with a bent angle of $\sim 18^{\circ}$ from the Ru– N bond. Owing to such asymmetric coordination bond lengths and structural distortion of the 8pyq ligand, the extent of the π conjugation in a ligand would be decreased. These structural features of $[Ru(dmb)_2(8pyq)]^{2+}$ have a large influence on the electrochemical and spectroscopic properties of the complex.

Cyclic Voltammograms. Figure 2 shows cyclic voltammograms of the complex in CH₃CN containing 0.1 M TBAPF₆ at 298 K together with those of the reference complexes $[Ru(dmb)_2(bpy)]^{2+}$ and $[Ru(bpy)_3]^{2+}$. The redox potentials of the complexes are summarized in Table 2. The complexes showed a quasi-reversible wave responsible for the $\hat{R}u^{III/II}$ redox couple at +1.16 to +1.32 V vs SCE (saturated calomel electrode, -0.42 V vs ferrocenium/ferrocene redox couple under the experimental conditions). The oxidation potential of $[\text{Ru}(\text{dmb})_2(\text{bpy})]^{2+}$ ($E_{\text{ox}} = +1.21$ V) was more negative than that of $[\text{Ru}(\text{bpy})_3]^{2+}$ (+1.32 V), indicative of an increase in the electron density on the ruthenium(II) center by the presence of the electron-donating methyl groups in the dmb ligands. The E_{ox} value of $[Ru(dmb)_2(8pyq)]^{2+}$ (+1.16 V) was shifted in the negative potential direction compared to those of the reference complexes. The Ru^{III/II} redox couple of a polypyridyl ruthenium(II) complex is typically originated in the t_{2g} orbital of the ruthenium(II) center. Therefore, the negative potential shift of the E_{ox} obtained for $[Ru(dmb)_2(8pyq)]^{2+}$ is explainable by a decrease in the extent of the ligand-field splitting owing to the six-membered chelate structure, longer Ru(II)-8pyq coordination bond lengths, and/or asymmetric nature of the 8pyq ligand.



Figure 2. Cyclic voltammograms of $[Ru(dmb)_2(8pyq)]^{2+}$ (black), $[Ru(dmb)_2(bpy)]^{2+}$ (green), and $[Ru(bpy)_3]^{2+}$ (red) in CH₃CN containing 0.1 M TBAPF₆ at 298 K. Yellow and gray curves represent those of ferrocene and neat electrolyte solution under identical conditions, respectively.

Table 2. Redox Potentials of the Complexes in CH_3CN Containing 0.1-M TBAPF₆

potential/V vs SCE			
-1.80	-1.57	-1.25	+1.16
-1.81	-1.58	-1.36	+1.21
-1.75	-1.50	-1.30	+1.32
	-1.80 -1.81 -1.75	potential/ -1.80 -1.57 -1.81 -1.58 -1.75 -1.50	potential/V vs SCE -1.80 -1.57 -1.25 -1.81 -1.58 -1.36 -1.75 -1.50 -1.30

All the complexes showed three redox waves responsible for successive ligand reductions. Because the second $(E_{\rm red2} = -1.57 \text{ V})$ and third $(E_{\rm red3} = -1.80 \text{ V})$ reduction potentials of $[\text{Ru}(\text{dmb})_2(8\text{pyq})]^{2+}$ were almost identical to those of $[\text{Ru}(\text{dmb})_2(\text{bpy})]^{2+}$ (-1.58 and -1.81 V, respectively), they can be ascribed to the reductions of the ancillary dmb ligands. Thus, the first reduction potentials $(E_{\rm red1})$ of the complexes correspond to the reductions of the acceptor ligand in a complex (i.e., 8pyq and bpy). The $E_{\rm red1}$ value of $[\text{Ru}(\text{dmb})_2(8pyq)]^{2+}$ (-1.25 V) was obtained at the more positive potential region than that of $[\text{Ru}(\text{dmb})_2(\text{bpy})]^{2+}$ (-1.36 V), reflecting a stabilization of the π^* orbital of the acceptor ligand in energy presumably due to large π -conjugation system of the 8pyq ligand. In addition, the redox wave for the acceptor-ligand reduction of $[\text{Ru}(\text{dmb})_2(8pyq)]^{2+}$ was less reversible than those of $[\text{Ru}(\text{dmb})_2(\text{bpy})]^{2+}$. The

reversibility was not improved even by a potential sweep between -0.26 and -1.42 V. The result indicates a structural change upon one-electron reduction of $[Ru(dmb)_2(8pyq)]^{2+}$. In practice, an optimized geometry of the reduced form of the complex (i.e., $[Ru(dmb)_2(8pyq)]^+$) suggests the structural change upon one-electron reduction, as shown in Figure S1. These differences in the redox potentials between the complexes strongly suggest that the spectroscopic properties of a $[Ru(dmb)_2L]^{2+}$ complex are also controllable by varying the acceptor ligand L.

Absorption and Emission Spectra. Figure 3 shows absorption spectra of the complexes in CH₃CN at 298 K, and



Figure 3. Absorption spectra of $[Ru(dmb)_2(8pyq)]^{2+}$ (black), $[Ru(dmb)_2(bpy)]^{2+}$ (green), and $[Ru(bpy)_3]^{2+}$ (red) in CH₃CN at 298 K.

Table 3. Spectroscopic Properties of the Complexes in CH₃CN at 298 K

complex	$\lambda_{\rm abs}/{\rm nm}~(\varepsilon/10$	$0^4 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\rm em}/{\rm nm}$	$\Phi_{\rm em}{}^a$
$[Ru(dmb)_2(8pyq)]^{2+}$	284 (6.4)	432 (1.0)	630	0.004
$[Ru(dmb)_2(bpy)]^{2+}$	286 (7.7)	456 (1.3)	637	0.095
$[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$	287 (8.0)	451 (1.4)	619	(0.095)
^{<i>a</i>} Determined using [Ri = 0.095).	u(bpy) ₃](PF ₆) ₂ in CH ₃ CN	as a stand	dard (Φ_{em}

the spectroscopic properties are summarized in Table 3. Although an intense ligand-centered $\pi\pi^*$ band was observed at around 285 nm, irrespective of the ligand structure, the band of $[\text{Ru}(\text{dmb})_2(8\text{pyq})]^{2+}$ was relatively broad, and the molar absorption coefficient at the maximum wavelength ($\varepsilon = 6.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 284 nm) was smaller than those of the reference complexes ($\sim 8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Such a spectral difference is explainable by the heteroleptic π -system of $[\text{Ru}(\text{dmb})_2(8\text{pyq})]^{2+}$.

The MLCT absorption band observed in the visible region depended on the acceptor ligand more strongly. The MLCT absorption maximum wavelength of $[Ru(dmb)_2(8pyq)]^{2+}$ (λ_{abs} = 432 nm) was much shorter, and the corresponding ε value (1.0 × 10⁴ M⁻¹ cm⁻¹) was smaller than that of [Ru(dmb)_2(bpy)]^{2+} (1.3 × 10⁴ M⁻¹ cm⁻¹ at 456 nm) or

 $[{\rm Ru}({\rm bpy})_3]^{2+}$ (1.4 \times 10⁴ M⁻¹ cm⁻¹ at 451 nm). Furthermore, $[{\rm Ru}({\rm dmb})_2({\rm 8pyq})]^{2+}$ exhibited the absorption band even in longer-wavelength region than the MLCT absorption maximum and, therefore, the spectral band shape of $[{\rm Ru}-({\rm dmb})_2({\rm 8pyq})]^{2+}$ at >370 nm was significantly different from those of the reference complexes. Although, in absorption spectra of the polypyridyl ruthenium(II) complexes, the ³MLCT band is observable at >500 nm as a shoulder of singlet band owing to the spin—orbit coupling, the ε value of $[{\rm Ru}({\rm dmb})_2({\rm 8pyq})]^{2+}$ in a longer-wavelength region is larger than that of typical ³MLCT band (<10³ M⁻¹ cm⁻¹). To reveal the origin of the difference in the MLCT band between the complexes, the MLCT absorption maximum energies $(E_{\rm abs})$ were plotted against the $(E_{\rm ox}-E_{\rm red1})$ values obtained by the electrochemical measurements (Figure 4) together with those



Figure 4. Plot for the absorption maximum energy versus $(E_{ox} - E_{red1})$ value of the complexes in CH₃CN at 298 K. Black, green, and red squares correspond to $[\text{Ru}(\text{dmb})_2(\text{8pyq})]^{2+}$, $[\text{Ru}(\text{dmb})_2(\text{bpy})]^{2+}$, and $[\text{Ru}(\text{bpy})_3]^{2+}$, respectively. Gray squares represent the data for $[\text{Ru}(\text{NN})_3]^{2+}$ complexes taken from ref 36. Black line is a linear regression for the data except for $[\text{Ru}(\text{dmb})_2(\text{8pyq})]^{2+}$.

of reported homoleptic polypyridyl ruthenium(II) ([Ru-(NN)₃]²⁺) complexes.³⁶ Because a change in the electronic configuration upon the MLCT transition can be described as $d\pi^6 \rightarrow d\pi^5 \pi^{*1}$, the $E_{\rm abs}$ value typically correlates to a difference between the metal oxidation (Ru^{III/II}) and ligand reduction ($L^{0,\bullet-}$) potentials (i.e., the ($E_{\rm ox} - E_{\rm red1}$) value). In practice, a good linear correlation was found for the typical complexes, including [Ru(dmb)₂(bpy)]²⁺ and [Ru(bpy)₃]²⁺. On the basis of the linear regression in Figure 4, the $E_{\rm abs}$ value of [Ru(dmb)₂(8pyq)]²⁺ was larger by ~0.25 eV than that expected from the ($E_{\rm ox} - E_{\rm red1}$) value. The result indicates that the absorption shoulder observed in the longer-wave-length region observed for [Ru(dmb)₂(8pyq)]²⁺ is assigned to the lowest-energy singlet MLCT transition to the 8pyq ligand. Further details are discussed in the following section.

Corrected emission spectra of the complexes in CH₃CN at 298 K are shown in Figure 5. The emission maximum wavelengths (λ_{em}) and the emission quantum yields (Φ_{em})



Figure 5. Corrected emission spectra of $[Ru(dmb)_2(8pyq)]^{2+}$ (black), $[Ru(dmb)_2(bpy)]^{2+}$ (green), and $[Ru(bpy)_3]^{2+}$ (red) in CH₃CN at 298 K (excitation wavelength = 450 nm).

determined by the relative method using $[Ru(bpy)_3](PF_6)_2$ in CH₃CN at 298 K as a standard are summarized in Table 3. The emission spectrum of $[Ru(dmb)_2(8pyq)]^{2+}$ was broad and featureless, indicative of a phosphorescence from the ³MLCTtype excited state. The $\hat{\Phi}_{em}$ value of $[Ru(dmb)_2(8pyq)]^{2+}$ (0.004) was quite low compared with those of the reference complexes (0.095). Because the structure of [Ru- $(dmb)_2(8pyq)$ ²⁺ is distorted around the 8pyq ligand and changes upon one-electron reduction of the 8pyq ligand, as suggested by the theoretical calculation and electrochemical measurements, accelerated thermal deactivation to the ground state is expected. In addition, weak singlet MLCT absorption indicates a decelerated radiative process as documented as the Strickler-Berg relation for both organic compounds³⁷ and transition metal complexes.³⁸ Therefore, accelerated nonradiative decay and decelerated radiative processes would result in the weak emission from $[Ru(dmb)_2(8pyq)]^{2+}$. The slightly higher-energy emission of $[Ru(dmb)_2(8pyq)]^{2+}$ $(\lambda_{em} =$ 630 nm) than that of $[Ru(dmb)_2(bpy)]^{2+}$ ($\lambda_{em} = 637$ nm) seems to be contradictory to the lower-energy singlet MLCT absorption. The energy difference between the absorption and emission of a phosphorescent transition metal complex is dominated by an extent of intersystem crossing and inner-/ outer-sphere relaxations in the triplet excited states. The structural change in the excited state indicated by the electrochemical measurements for [Ru(dmb)₂(8pyq)]²⁺ generally results in large reorganization energy and, therefore, it is indicated that [Ru(dmb)₂(8pyq)]²⁺ exhibits a small singlettriplet energy gap (ΔE_{ST}). Because ΔE_{ST} is an important factor to control an emissivity of the transition metal complexes as we have reported, a class of the complexes possessing a sixmembered chelate structure might be a potential candidate for the future emitting materials. Although we performed the TD-DFT calculations for the ground-state optimized geometries of the complexes, small ΔE_{ST} for $[Ru(dmb)_2(8pyq)]^{2+}$ was, unfortunately, not evidenced (see Table S3), presumably due to a lack of considerations of the geometrical changes in the triplet excited states. Thus, further detailed photophysical measurements and understanding will be completed by a development of intensely emissive derivatives because the

emission from $[Ru(dmb)_2(8pyq)]^{2+}$ is quite weak (Φ_{em} = 0.004).

Theoretical Calculations. To evaluate the molecular orbitals (MOs) and absorption transitions of [Ru- $(dmb)_2(8pyq)$]²⁺ in detail, the DFT/TD-DFT calculations were carried out for the complexes. Selected calculated excited states (S_1 - S_{10} and S_{11} - S_{50} with an oscillator strength (f) being >0.01) of the complexes are summarized in Tables S4–S6. Figure 6 (>320 nm region) and Figure S2 (full wavelength



Figure 6. Comparisons of the absorption spectra (>320 nm region) and oscillator strengths calculated by TD-DFT (perpendicular bars) of $[Ru(dmb)_2(8pyq)]^{2+}$ (a), $[Ru(dmb)_2(bpy)]^{2+}$ (b), and $[Ru(bpy)_3]^{2+}$ (c). The transition energies calculated by TD-DFT were shifted to lower energy by 5% to correct the overestimation.

region) show comparisons of the observed absorption spectra and singlet absorption transitions obtained by the TD-DFT calculations, in which transition energies obtained by TD-DFT were shifted to lower energy by 5%. Although transition energies were overestimated by ~5%, the calculated transitions reproduced the experimentally observed spectra of the complexes well. Furthermore, as compared in Figure 7, energies of both the highest-energy occupied MO (HOMO) and lowest-energy unoccupied MO (LUMO) of the complexes qualitatively correlated to the oxidation ($E_{\rm ox}$) and first reduction potentials ($E_{\rm red1}$), respectively. Therefore, the adequacy of our calculations is supported.

As summarized in Tables S4–S6, the lowest-energy singlet excited state (S_1) of $[Ru(dmb)_2(8pyq)]^{2+}$ is ascribed to a HOMO \rightarrow LUMO(55%)/LUMO+1(25%)/LUMO+2(20%) transition, whereas those of the reference complexes are based on HOMO \rightarrow LUMO/LUMO+1 transitions. Tables S7–S9 summarize frontier MO populations of the complexes, and Figure 8 shows natural transition orbitals (NTOs) to generate



Figure 7. Redox potentials (left) and MO energies (right) of $[\text{Ru}(\text{dmb})_2(8\text{pyq})]^{2+}$ (black), $[\text{Ru}(\text{dmb})_2(\text{bpy})]^{2+}$ (green), and $[\text{Ru}(\text{bpy})_3]^{2+}$ (red). Filled symbols represent the oxidation potentials (i.e., E_{ox}) or occupied MOs (i.e., HOMO, HOMO–1, and HOMO–2), and hollow ones represent the reduction potentials (i.e., $E_{\text{red1-3}}$) or unoccupied MOs (i.e., LUMO, LUMO+1, and LUMO+2).

 S_1 of the complexes. These results indicate that S_1 of $[{\rm Ru}({\rm dmb})_2({\rm bpy})]^{2+}$ or $[{\rm Ru}({\rm bpy})_3]^{2+}$ is assigned to the MLCT excited state in which the excited electron is localized at byy ligand(s). On the other hand, the hole of $[{\rm Ru}({\rm dmb})_2({\rm 8pyq})]^{2+}$ distributes mainly to the 8pyq ligand with a

minor contribution of a dmb ligand. Thus, a transition dipole moment to give the lowest-energy MLCT excited state decreases. Because the oscillator strength of a CT transition proportionally correlates to a square of the transition dipole moment, $[Ru(dmb)_2(8pyq)]^{2+}$ has shown weak absorption at the longer-wavelength region. The contribution of higherenergy π^* orbital of one of two dmb ligands is originated presumably in a decreased HOMO–LUMO overlap by the bent coordination of the quinoline moiety, as discussed in the optimized geometry.

CONCLUSIONS

A novel polypyridyl ruthenium(II) complex with a sixmembered chelate ring ($[Ru(dmb)_2(8pyq)]^{2+}$) was synthesized, and the effects of the chelate structure and coordination geometry on the electrochemical/spectroscopic properties of a complex were evaluated in detail. The theoretical calculations suggested a significant influence of an introduction of a sixmembered chelate structure on the coordination sphere, and the steric displacement of the coordinating nitrogen atoms was closer to the ideal octahedral geometry than that of the reference complexes. Owing to such a structural difference, the oxidation potential was shifted to the negative potential direction, indicative of a decrease in the extent of the ligandfield splitting, and relatively intense MLCT absorption in the



Figure 8. NTOs for the lowest-energy singlet excited states (S₁) of the complexes in CH₃CN (contour = 0.03 eÅ⁻³).

longer-wavelength region was observed for $[Ru-(dmb)_2(8pyq)]^{2+}$ compared with the reference complexes without any six-membered chelate rings. Although intense absorption in the broad UV–visible is advantageous for the applications as photosensitizers, the emission from $[Ru-(dmb)_2(8pyq)]^{2+}$ was quite weak, presumably due to the structural distortion of the 8pyq ligand in the complex. On the basis of the results obtained in the present study, new and novel light absorbers/triplet emitters will be developed in the near future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00924.

Synthesis and detailed results of theoretical calculations (PDF)

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Notes

The authors declare no competing financial interest.

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