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Photophysical Properties and Excitation Polarization of *fac*/*mer*-Ruthenium Complexes with 5′-Amino-2,2′-bipyridine-5-carboxylic Acid Derivatives

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Novel ruthenium(II) complexes, *fac*/*mer*-[Ru(MeCO-**5Bpy**-R)$_3$]$^{2+}$ (H-**5Bpy**-OH = 5′-amino-2,2′-bipyridine-5-carboxylic acid; R = –NH^{t}Bu, –NH(*c*Hex), –N(*c*Hex)$_2$), have been synthesized. The fac and mer isomers have been successfully separated using HPLC techniques, and their photophysical/electrochemical properties have been investigated. In the absorption and emission spectra of *fac*/*mer*-[Ru(MeCO-**5Bpy**-R)$_3$]$^{2+}$ with secondary amines (R = –N(*c*Hex)$_2$) in acetonitrile at room temperature, the maximum wavelengths based on the MLCT are longer than those for the amide derivatives with primary amines (R = –NH^{t}Bu, –NH(*c*Hex)). A small solvent effect on the photophysical properties between *fac*- and *mer*-[Ru(MeCO-**5Bpy**-NH^{t}Bu)$_3$]$^{2+}$ has been observed. The excitation polarization spectra, giving *P* values reflecting the relation between the absorption and the emission oscillators, for the *fac*- and *mer*-ruthenium(II) complexes (C_3 and C_1 symmetry, respectively) have been measured for the first time. Almost no difference in the excitation polarization spectra between the fac and mer complexes is found, and these spectra are similar to that for [Ru(bpy)$_3$]$^{2+}$ with D_3 symmetry. This finding suggests that the orientations of the absorption and emission oscillators, in the case of the ruthenium(II) tris(2,2′-bipyridine) derivatives, would not be affected by the symmetries of the complexes and that the *P* values for any derivatives would be similar to that for [Ru(bpy)$_3$]$^{2+}$.

Introduction

De novo design peptides have attracted much attention from the viewpoint of searching for functional molecules.[1−4] In the designs, the bipyridyl group has frequently been used as the binder with metal ions to form α-helical peptide bundles[5−8] or collagenous peptides.[9] Imperiali et al. synthesized unnatural α-amino acids with a bipyridyl group side chain.[10] They further designed sensor peptides containing two residues of 5′-amino-2,2′-bipyridine-5-carboxylic acid (H-**5Bpy**-OH) for metal ions.[11] We have also designed artificial proteins, the peptidesof which contain three residues of **5Bpy**.[12] The peptides would coordinate with a metal ion, producing an octahedral metal complex with a definite folding structure of the small proteins. If the ruthenium(II) ion was used, the artificial proteins should possess the ruthenium(II) tris(2,2′-bipyridyl)-type complex as the core, and they were expected to show some photochemical functions such as emission, photoinduced electron/energy transfer, and photocatalysis. To predict the photochemical functions of the artificial proteins, we have investigated the photophysical properties of the ruthenium(II) tris-chelate complexes with symmetrical ligands bearing amide groups, −CONHR or −NHCOR, at the 5,5′-positions in 2,2′-

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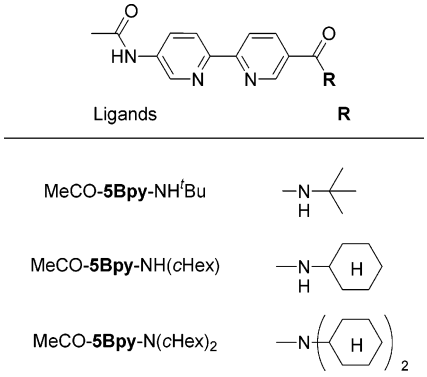

Figure 1. Unnatural amino acid derivatives.

bipyridine.[12] We have preliminarily found that the orientation of the amide groups strongly affects the photophysical properties of these ruthenium(II) complexes. In this paper, we discuss the photophysical properties of the ruthenium(II) tris-chelate complexes with the unnatural amino acid derivatives (Figure 1), in which the N and C termini in **5Bpy** are amidated, as model complexes for artificial (metallo)-proteins.

The ruthenium(II) tris-chelate complexes with the unnatural amino acid derivatives have two isomers (i.e., facial (fac) and meridional (mer) complexes) because of the unsymmetrical ligands. Although the difference in the photophysical properties between the *fac*- and the *mer*-ruthenium(II) complexes with the unsymmetrical ligands has been interesting, there have been very few reports until now.[13] Recently, Fletcher et al. reported the separation of the two isomers of the ruthenium(II) tris-chelate complexes with 2,2′-bipyridine-5-carboxylic acid ester derivatives.[14,15] They further described that almost no difference in the photophysical properties between the two isomers has been found. Furthermore, the fac/mer ratio in the syntheses of metal tris-chelate complexes has attracted attention because of the supramolecular architectures functionalized with polypyridine complexes.[16] The statistical ratio between the fac and mer complexes is considered to be 25:75.[8,17,18] To selectively obtain the fac isomer, Weizman et al. reported a template method using 1,3,5-tris(hydroxymethyl)-benzene attached to three molecules of EtOCO-**5Bpy**-Ala-OH.[17] Fletcher et al. also reported a selective synthesis of the fac isomer using tripodal bipyridyl ligand systems with removable templates.[19] For the selective syntheses of the mer isomer, Fletcher et al. used the 5-substituent-2,2′-bipyridine with a bulky group, such as *tert*-butyl, involving steric hindrance.[18] We also recently reported that the iron(II) tris-chelate complexes with the unnatural amino acid derivatives, Ac-**5Bpy**-NR_2, produced the mer isomers selectively.[20]

The excitation polarization measurements for the *fac*/*mer*-ruthenium(II) tris-chelate complexes with the unsymmetrical bipyridyl ligand complexes have not been reported until now. The excitation polarization measurement can give information on the relationship between the absorption and emission oscillators, reflecting the symmetries of the excited states. Because the fac and mer complexes have different symmetries (the fac and mer complexes have C_3 and C_1 symmetries, respectively), the excitation polarization spectra of the two isomers might be different. The excitation polarization measurement for $[Ru(bpy)_3]^{2+}$ was first reported by Fujita and Kobayashi,[21] in which they presented excitation polarization spectra at the metal-to-ligand charge transfer (MLCT) band. Felix et al. extended the discussion to the ultraviolet region.[22] DeArmond et al. also investigated the excitation polarization spectra for $[Ru(bpy)_3]^{2+}$, as well as other related transition metal complexes.[23−32] They measured the excitation polarization spectra of *cis*/*trans*-$[Ru(bpy)_2(L)_2]^{2+}$ (L = py or phosphine derivatives) and reported that the spectra are different between the cis and trans isomers.[31] For $[(bpy)_2Ru(5,5′\text{-phenyleneethynylene-bpy})]^{2+}$, which is the ruthenium(II) complex with 5,5′-disubstituented-2,2′-bipyridine, the excitation polarization spectrum was recently reported by Wang et al.[33] However, there is no report on the excitation polarization spectra for the fac and mer isomers of the ruthenium(II) tris-chelate complexes with unsymmetrical bipyridyl ligands.

In this paper, we report the syntheses of novel ruthenium(II) tris-chelate complexes with unnatural amino acid derivatives, MeCO-**5Bpy**-R (R = −NH^{t}Bu, −NH(*c*Hex), −N(*c*Hex)$_2$) and the separation of the fac and mer isomers. We further discuss the electrochemical/photophysical properties and the excitation polarization results for the *fac*- and *mer*-ruthenium(II) complexes.

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Experimental Section

General. Reagent grade chemicals were purchased from Aldrich Chemical Co., Ltd., or Wako Pure Chemical Industries, Ltd. Acetonitrile, ethanol, methanol, and diethyl ether were distilled over CaH_2 under Ar before use. Reagent grade isopentane was purchased from Wako Pure Chemical Industries, Ltd., and was used without further purification.

^1H and ^{13}C NMR spectra were measured with a JEOL JNM EX-400 and a Bruker ARX-300. Elementary analyses were carried out with a Perkin-Elmer Series II CHNS/O Analyzer 2400. EI-MS measurements were carried out with a Hitachi M-2500 mass spectrometer. FT-IR spectra were measured with a Perkin-Elmer Model 1600 spectrometer. Analytical HPLC was performed on a Shimadzu CLASS−vP V6.12 SP2 instrument equipped with a Tosoh TSKgel ODS-80Ts column (4.6 mm $\phi \times$ 15 cm) and a TSKguardgel ODS-80Ts column (3.2 mm $\phi \times$ 1.5 cm). Preparative HPLC was carried out using a Japan Analytical Industry recycling preparative HPLC LC-918RU with a Nacalai Tesque COSMOSIL $5C_{18}$-AR−II packed column (10 mm $\phi \times$ 250 mm) and a COSMOSIL $5C_{18}$-AR−II guard column (10 mm $\phi \times$ 20 mm). H_2O/CH_3CN (0.1% TFA) solutions were used as eluents.

Syntheses of Ligands. MeCO-**5Bpy**-OH, the starting material for the unnatural amino acid derivatives, was synthesized according to the literature.[12,34]

MeCO-5Bpy-NH^{t}Bu. MeCO-**5Bpy**-OH (200 mg, 0.78 mmol) was refluxed in $SOCl_2$ (5.0 cm^3) for 1 h. The solution was evaporated and was then dried under vacuum. The acid chloride obtained was refluxed with *tert*-butylamine (0.20 cm^3, 3.9 mmol) in benzene (5.0 cm^3) for 30 min. The solution was evaporated; the residue was then washed with water and dried under vacuum. The obtained crude solid was dissolved in methanol, and the mixture was filtered. The filtrate was evaporated, and the solid was washed with ether and CH_2Cl_2 and then dried in vacuo. Yield: 58%. IR (KBr, cm^{-1}): 3700−3200, 2972.6, 1672.1, 1632.2. ^1H NMR (300 MHz, DMSO-d_6): δ 10.373 (s, 1H), 8.983 (s, 1H), 8.828 (d, J = 2.1 Hz, 1H), 8.354 (t, 2H), 8.264−8.191 (m, 2H), 8.032 (s, 1H), 2.104 (s, 3H), 1.391 (s, 9H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 169.017, 164.413, 156.156, 148.574, 148.154, 139.830, 136.736, 136.242, 130.483, 126.573, 121.227, 119.074, 51.115, 28.578, 23.991. MS *m*/*z* (EI): 312 (calcd 312.37). Anal. Calcd for $C_{17}H_{20.5}N_4O_{2.25}$ (0.25 H_2O): C, 64.44; H, 6.52; N, 17.68. Found: C, 64.53; H, 6.46; N, 17.84.

MeCO-5Bpy-NH(*c*Hex). MeCO-**5Bpy**-NH(*c*Hex) was synthesized from MeCO-**5Bpy**-OH (200 mg, 0.78 mmol) and cyclohexylamine (0.32 cm^3, 3.94 mmol) in a manner similar to that used for MeCO-**5Bpy**-NH^{t}Bu. The crude compound was purified by washing with 5% $NaHCO_{3aq}$, water, ether, CH_2Cl_2, and cold methanol. Yield: 57%. IR (KBr, cm^{-1}): 3700−3200, 2932.7, 2854.6, 1665.6, 1630.5. ^1H NMR (300 MHz, DMSO-d_6): δ 10.360 (s, 1H), 9.028 (s, 1H), 8.829 (d, J = 2.1 Hz, 1H), 8.442−8.189 (m, 5H), 3.783 (br, 1H), 2.104 (s, 3H), 1.786 (dbr, J = 29.2 Hz, 4H), 1.605 (dbr, J = 11.9 Hz, 1H), 1.310 (m, 4H), 1.144 (br, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 168.918, 163.531, 156.626, 148.781, 148.178, 139.921, 136.646, 135.936, 129.411, 126.350, 121.095, 119.041, 48.426, 32.375, 25.253, 24.890, 23.958. MS *m*/*z* (EI): 338 (calcd 338.17). Anal. Calcd for $C_{19}H_{22.67}N_4O_{2.33}$ (1/3H_2O): C, 66.06; H, 6.43; N, 16.51. Found: C, 66.15; H, 6.52; N, 16.35.

MeCO-5Bpy-N(*c*Hex)$_2$. MeCO-**5Bpy**-N(*c*Hex)$_2$ was synthesized from MeCO-**5Bpy**-OH (310 mg, 1.21 mmol) and dicyclohexylamine (1.01 cm^3, 6.03 mmol) in a manner similar to that used for MeCO-**5Bpy**-NH^{t}Bu. The crude material was purified by column chromatography (Wako gel C-200, 5 cm $\phi \times$ 26 cm, 10% MeOH/$CHCl_3$). The solid obtained was washed with water, cold methanol, and benzene. Yield: 47%. IR (KBr, cm^{-1}): 3422.1, 3279.1, 2928.4, 2856.7, 1696.2, 1613.0. ^1H NMR (300 MHz, DMSO-d_6): δ 8.820 (br, 1H), 8.490 (t, 1H), 8.442 (d, J = 2.7 Hz, 1H), 8.138 (t, 2H), 7.926 (dd, J = 8.7, 2.1 Hz, 1H), 7.606 (dd, J = 8.1, 2.1 Hz, 1H), 3.365 (br, 1H), 3.126 (br, 1H), 2.613 (br, 2H), 2.243 (s, 3H), 2.100−0.900 (m, 18 H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 169.184 (d), 155.807, 151.080, 145.459 (d), 140.965 (d), 135.175, 133.682 (d), 133.311, 127.916 (d), 121.094 (d), 120.153 (d), 31.323−24.220 (m). MS *m*/*z* (EI): 420 (calcd 420.25). Anal. Calcd for $C_{25}H_{32}N_4O_2$: C, 71.40; H, 7.67; N, 13.32. Found: C, 71.57; H, 7.81; N, 13.29.

Syntheses of Ruthenium Complexes. The ruthenium complexes were synthesized by heating (microwave irradiation for 1−2 min or reflux for 15 min) an ethylene glycol solution of $RuCl_3 \cdot nH_2O$ (n = 1−3) with 3 or 4 equiv of ligand. The microwave irradiation was carried out in a household electronic oven, Mitsubishi RR-M1 (50 Hz, 600 W), to which an Allihn condenser was attached according to the literature.[35] The red solution obtained was filtered to remove unreacted and insoluble materials, which were washed with a small amount of water. $NaPF_6$ (>10 molar equiv of ruthenium) dissolved in the smallest possible amount of water was added to the filtrate. The precipitate was collected by filtration and washed with cold water. The crude sample was acetylated with acetic anhydride because the acetyl groups at the N termini in the ruthenium(II) complexes obtained were partially deprotected in the case of microwave synthesis. The crude mixture of fac/mer complexes was separated and purified using preparative HPLC with H_2O/CH_3CN containing 0.1% TFA as eluent. Each fraction was neutralized with 5% $NaHCO_{3aq}$, and then, the acetonitrile in the solution was evaporated at room temperature. $NaPF_6$ in excess of the molar equivalent, dissolved in a small amount of water, was added to the resulting solution. The precipitate was collected by filtration, washed with cold water, and dried in vacuo, to yield a red solid powder.

[Ru(MeCO-5Bpy-NH^{t}Bu)$_3$](PF$_6$)$_2$. The crude sample was synthesized by microwave irradiation of an ethylene glycol solution of $RuCl_3 \cdot nH_2O$ (30.5 mg, 0.15 mmol) and MeCO-**5Bpy**-NH^{t}Bu (138 mg, 0.44 mmol). The fac/mer complexes were separated and purified using preparative HPLC with a 65% H_2O/CH_3CN solution containing 0.1% TFA as eluent (fac, 25 mg; mer, 66 mg). The fac complex. Yield: 19%. ^1H NMR (300 MHz, DMSO-d_6): δ 10.574 (br, 3H), 8.848 (d, J = 9.3 Hz, 3H), 8.749 (d, J = 8.7 Hz, 3H), 8.560 (dd, J = 8.6, 1.5 Hz, 3H), 8.313 (d, J = 2.1 Hz, 3H), 8.197 (s, 3H), 8.109 (dd, J = 8.9, 1.8 Hz, 3H), 7.998 (d, J = 1.5 Hz, 3H), 1.992 (s, 9H), 1.270 (s, 27H). Anal. Calcd for $C_{51}H_{64}F_{12}N_{12}O_8P_2Ru$ (2H_2O): C, 44.90; H, 4.73; N, 12.32. Found: C, 45.17; H, 4.79; N, 12.10. The mer complex. Yield: 34%. ^1H NMR (300 MHz, DMSO-d_6): δ 10.581 (s, 1H), 10.572 (s, 1H), 10.558 (s, 1H), 8.857 (dd, J = 9.2, 3.0 Hz, 3H), 8.777 (dd, J = 8.6, 3.6 Hz, 3H), 8.641 (m, 3H), 8.346 (d, J = 2.1 Hz, 1H), 8.282 (d, J = 2.4 Hz, 1H), 8.268 (d, J = 2.1 Hz, 1H), 8.190−8.136 (m, 4H), 8.100 (s, 2H), 7.981 (d, J = 1.8 Hz, 1H), 7.875 (s, 2H), 2.000 (s, 3H), 1.986 (s, 6H), 1.280 (s, 9H), 1.275 (s, 9H), 1.267 (s, 9H). Anal. Calcd for $C_{51}H_{64}F_{12}N_{12}O_8P_2Ru$ (2H_2O): C, 44.90; H, 4.73; N, 12.32. Found: C, 45.13; H, 4.81; N, 12.28.

[Ru(MeCO-5Bpy-NH(*c*Hex))$_3$](PF$_6$)$_2$. The crude sample was synthesized by microwave irradiation of an ethylene glycol solution

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of $RuCl_3 \cdot nH_2O$ (20 mg, 9.83×10^{-2} mmol) and MeCO-**5Bpy**-NH(*c*Hex) (100 mg, 0.30 mmol). The fac/mer complexes were separated and purified using preparative HPLC with a 60% H_2O/CH_3CN solution containing 0.1% TFA as eluent. The mer complexes were further purified using preparative HPLC with a 68% H_2O/CH_3CN solution containing 0.1% TFA as eluent (fac, 14 mg; mer, 40 mg). The fac complex. Yield: 10%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.609 (br, 3H), 8.823 (d, $J = 9.0$ Hz, 3H), 8.763 (d, $J = 8.4$ Hz, 3H), 8.665 (d, $J = 7.5$ Hz, 6H), 8.532 (dd, $J = 8.6$, 1.8 Hz, 3H), 8.345 (d, $J = 2.1$ Hz, 3H), 8.126 (dd, $J = 9.0$, 2.1 Hz, 3H), 7.999 (d, $J = 1.5$ Hz, 3H), 3.612 (br, 3H), 1.996 (s, 9H), 1.800−1.500 (br, 15H), 1.850−1.000 (br, 15 H). Anal. Calcd for $C_{57}H_{68}F_{12}N_{12}O_7P_2Ru$ ($1H_2O$): C, 48.07; H, 4.81; N, 11.80. Found: C, 48.14; H, 4.90; N, 11.68. The mer complex. Yield: 29%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.602 (br, 3H), 8.850−8.767 (m, 6H), 8.614 (t, 6H), 8.345 (d, $J = 1.8$ Hz, 1H), 8.264 (d, $J = 1.5$ Hz, 2H), 8.198 (t, 3 H), 8.010 (s, 1H), 7.940 (s, 1H), 7.882 (s, 1H), 3.614 (br, 3H), 2.004 (s, 3H), 1.986 (s, 6H), 1.800−1.500 (br, 15H), 1.350−1.000 (br, 15 H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 169.611 (d), 160.894 (t), 158.008 (d), 150.357 (t), 149.524 (d), 140.705 (d), 139.338 (t), 135.495 (d), 131.253 (t), 126.136 (t), 125.691 (d), 122.679 (t), 48.748, 32.125, 25.129, 24.733, 24.082. Anal. Calcd for $C_{57}H_{68}F_{12}N_{12}O_7P_2Ru$ ($1H_2O$): C, 48.07; H, 4.81; N, 11.80. Found: C, 47.78; H, 4.91; N, 11.69.

[Ru(MeCO-5Bpy-N(*c*Hex)$_2$)$_3$](PF$_6$)$_2$. The crude sample was synthesized by microwave irradiation of an ethylene glycol solution of $RuCl_3 \cdot nH_2O$ (31 mg, 0.15 mmol) and MeCO-**5Bpy**-N(*c*Hex)$_2$ (200 mg, 0.48 mmol). The obtained fac/mer complexes were separated and purified using preparative HPLC with a 37% H_2O/CH_3CN solution containing 0.1% TFA as eluent. The mer complexes were further purified using preparative HPLC with a 42% H_2O/CH_3CN solution containing 0.1% TFA as eluent (fac, 17 mg; mer, 58 mg). The fac complex. Yield: 7%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.609 (br, 3H), 8.823 (d, $J = 9.0$ Hz, 3H), 8.763 (d, $J = 8.4$ Hz, 3H), 8.665 (d, $J = 7.5$ Hz, 6H), 8.532 (dd, $J = 8.6$, 1.8 Hz, 3H), 8.345 (d, $J = 2.1$ Hz, 3H), 8.126 (dd, $J = 9.0$, 2.1 Hz, 3H), 7.999 (d, $J = 1.5$ Hz, 3H), 3.612 (br, 3H), 1.996 (s, 9H), 1.800−1.500 (br, 15H), 1.850−1.000 (br, 15 H). Anal. Calcd for $C_{75}H_{100}F_{12}N_{12}O_8P_2Ru$ ($2H_2O$): C, 53.34; H, 5.97; N, 9.95. Found: C, 53.42; H, 6.25; N, 9.70. The mer complex. Yield: 24%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.602 (br, 3H), 8.850−8.767 (m, 6H), 8.614 (t, 6H), 8.345 (d, $J = 1.8$ Hz, 1H), 8.264 (d, $J = 1.5$ Hz, 2H), 8.198 (t, 3 H), 8.010 (s, 1H), 7.940 (s, 1H), 7.882 (s, 1H), 3.614 (br, 3H), 2.004 (s, 3H), 1.986 (s, 6H), 1.800−1.500 (br, 15H), 1.350−1.000 (br, 15 H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 169.611 (d), 160.894 (t), 158.008 (d), 150.357 (t), 149.524 (d), 140.705 (d), 139.338 (t), 135.495 (d), 131.253 (t), 126.136 (t), 125.691 (d), 122.679 (t), 48.748, 32.125, 25.129, 24.733, 24.082. Anal. Calcd for $C_{75}H_{100}F_{12}N_{12}O_8P_2Ru$ ($2H_2O$): C, 53.34; H, 5.97; N, 9.95. Found: C, 53.38; H, 6.04; N, 10.00.

Spectroscopy. The photophysical properties at room temperature (293 ± 0.5 K) were measured in acetonitrile. The sample solutions in quartz cuvettes were degassed by five freeze−pump−thaw cycles. Absorption and emission spectra were measured with a Shimadzu UV-2100S spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer equipped with a Hamamatsu R928 photomultiplier tube, respectively. Emission spectra at 77 K were recorded with a cylindrical cell (8 mm $\phi \times 190$ mm) in EPA (5:5:2 diethyl ether/isopentane/ethanol (v/v/v)) and EtOH/MeOH (4:1 (v/v)) glassy solution under Ar. The quantum yields were determined in acetonitrile from the emission spectra using $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.090$)[36] as the standard. The lifetime of the ruthenium complexes was measured with a Spectra-Physics Quanta-Ray MOPO-700 instrument excited at 355 nm with a Nd:YAG laser with a slit width of 5 nm and an HV of 400.

Electrochemistry. Cyclic voltammograms were measured with a BAS 100B electrochemical analyzer using a BAS MCA Microcell kit in acetonitrile at room temperature under N_2. The sample concentration was 5.0×10^{-4} mol dm^{-3}, and ^{n}Bu$_4$NPF$_6$ (0.10 mol dm^{-3}) was used as an electrolyte. The counter electrode was a BAS VC-2 Pt wire, the working electrode was a BAS SPTE platinum disk of 1.6 mm ϕ, and the reference electrode was a BAS RE−5 (Ag/Ag^+ (TBAP/acetonitrile), 490 mV vs NHE)) of 70×6.0 mm. The scan rate was 0.20 V s^{-1}. The redox potentials were indicated based on the ferrocene/ferricinium couple (Fc/Fc^+) in acetonitrile.

Excitation Polarization. Excitation polarization was measured using a cylindrical cell (4 mm $\phi \times 190$ mm) in an EtOH/MeOH (4:1 (v/v)) glassy solution at 77 K under Ar. It was recorded with a Hitachi F-4500 fluorescence spectrophotometer equipped with Hitachi sheet polarizers. The sample cell was immersed in liquid nitrogen in a Dewar flask and then fixed to the cell holder. The excited spectra were monitored at the maximum wavelength in the emission spectra at 77 K.

The P values as the degree of polarization are defined by

$$P = \frac{I_{\parallel} - I_{\perp}(I_{\parallel}'/I_{\perp}')}{I_{\parallel} + I_{\perp}(I_{\parallel}'/I_{\perp}')}$$

where $I_{\parallel}$ and $I_{\perp}$ are the respective intensities of the parallel and perpendicular polarized excitation spectra in the direction of the oscillating electric vector of the exciting light and $I_{\parallel}'$ and $I_{\perp}'$ are the respective intensities of the parallel and perpendicular polarized excitation spectra in the direction of the oscillating magnetic vector of the exciting light.[37]

Results and Discussion

Syntheses. The ligands, unnatural amino acid derivatives, were synthesized according to the literature.[12,34] The ruthenium(II) complexes were synthesized by reflux or microwave irradiation of ethylene glycol, followed by treatment with $NaPF_6$, and were obtained as PF_6 salts. The acetyl groups at the N termini in the obtained ruthenium(II) complexes were partly deprotected, and therefore, the complexes were acetylated again by treating with acetic anhydride. The fac/mer ratio is theoretically 25:75 for the ruthenium(II) tris-chelate complexes of unsymmetrical bipyridyl ligands.[8,17,18] The fac/mer ratios for $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ and $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH(c\text{Hex}))_3]^{2+}$ were approximately 25:75, judging from the HPLC, in both the reflux and microwave irradiation methods. The ratio for *fac*/*mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}N(c\text{Hex})_2)_3]^{2+}$ was 21:79 with microwave irradiation; however, it became 17:83 upon refluxing (see Supporting Information). The high selectivity for the mer complex was probably the result of the steric hindrance of the substitutents at the C termini in the fac complex. Similar phenomena were observed for the iron(II) complexes with the ligands.[20] The fac/mer complexes were separated and purified using preparative HPLC with a H_2O/CH_3CN solution containing 0.1% TFA as eluent. The purities, judged from the HPLC, were

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(37) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* **1962**, *37*, 2413−2420.

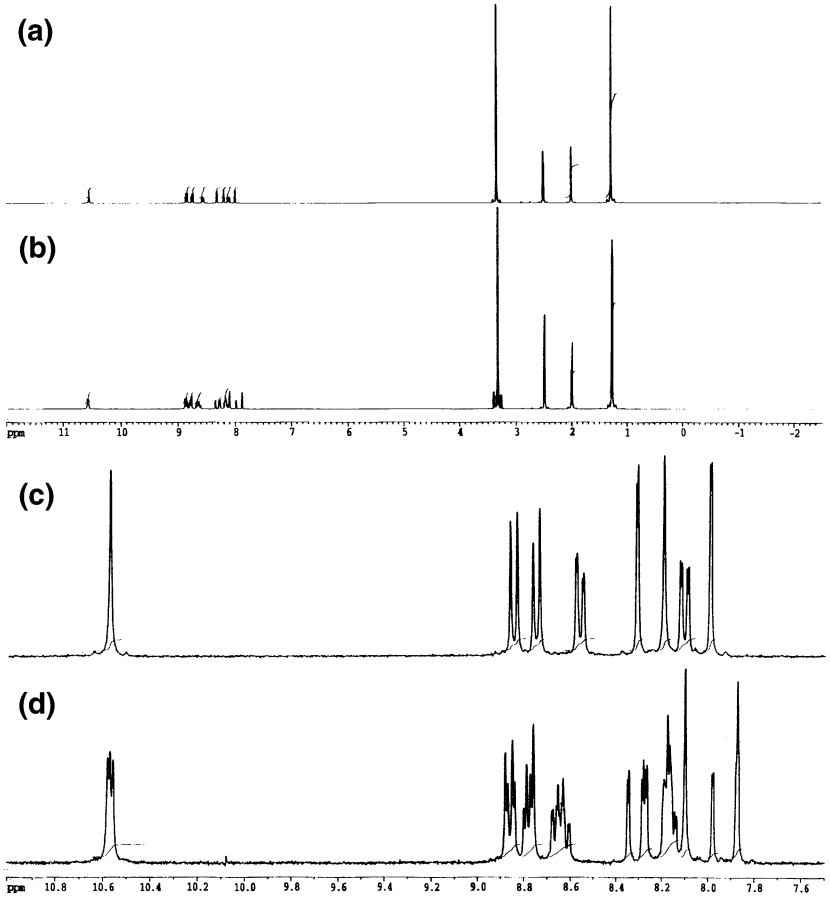

Figure 2. ^{1}H NMR spectra (300 MHz, DMSO-d_6) for *fac*/*mer*-[Ru(MeCO-**5Bpy**-NH^{t}Bu)$_3$]$^{2+}$: (a) fac complex, (b) mer complex, (c) aromatic region (7.5−11.0 ppm) for the fac complex, and (d) aromatic region (7.5−11.0 ppm) for the mer complex.

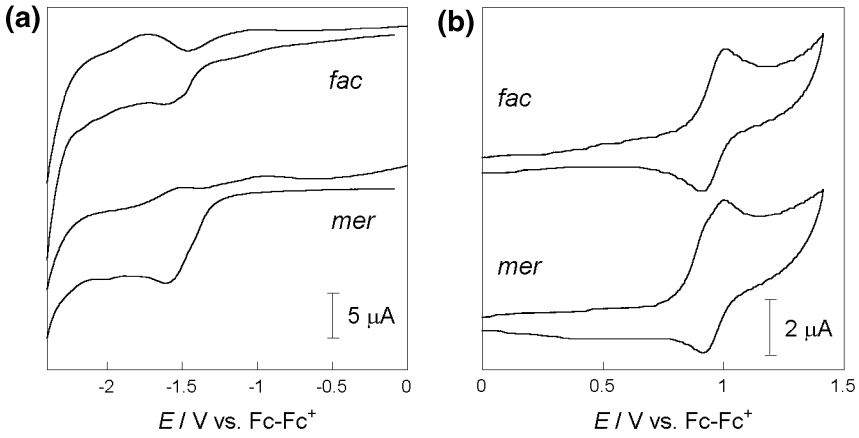

Figure 3. Cyclic voltammograms for (a) reduction and (b) oxidation of *fac*/*mer*-[Ru(MeCO-**5Bpy**-NH^{t}Bu)$_3$]$^{2+}$ (5.0×10^{-4} mol dm^{-3}) in CH_3CN containing ^{n}Bu$_4$NPF$_6$ (0.10 mol dm^{-3}) using a Pt electrode under N_2.

over 99% for each of the fac/mer isomers (see Supporting Information). As a typical result, the ^{1}H NMR spectra for the fac mer-complexes of [Ru(MeCO-**5Bpy**-NH^{t}Bu)$_3$]$^{2+}$ in DMSO-d_6 are shown in Figure 2. Three ligands in the fac complex were equivalent in the ^{1}H NMR spectrum because the fac complex has C_3 symmetry. On the other hand, the protons in the mer complex were unequivalently detected because it does not have a symmetrical axis (C_1 symmetry).

Electrochemistry. Cyclic voltammetry for fac/mer-[Ru(MeCO-**5Bpy**-NH^{t}Bu)$_3$]$^{2+}$ was carried out in acetonitrile containing ^{n}Bu$_4$NPF$_6$ as an electrolyte under N_2 using a Pt disk as a working electrode (Figure 3). The potentials are indicated based on ferrocene/ferricinium couple (Fc/Fc$^+$) in acetonitrile. These cyclic voltammograms were expected to be similar to that for [Ru(bpy)$_3$]$^{2+}$, which showed a reversible oxidation wave for Ru^{2+}/Ru^{3+} and three successive reduction waves corresponding to electrons entering the π^* orbitals in the bipyridyl ligands. Actually, reversible redox couples for Ru^{2+}/Ru^{3+} in both the fac and mer complexes were observed, as shown in Figure 3b. However, the reduction waves for these ruthenium(II) complexes were irreversible, and definite peaks were not detected (Figure 3a). This is probably the

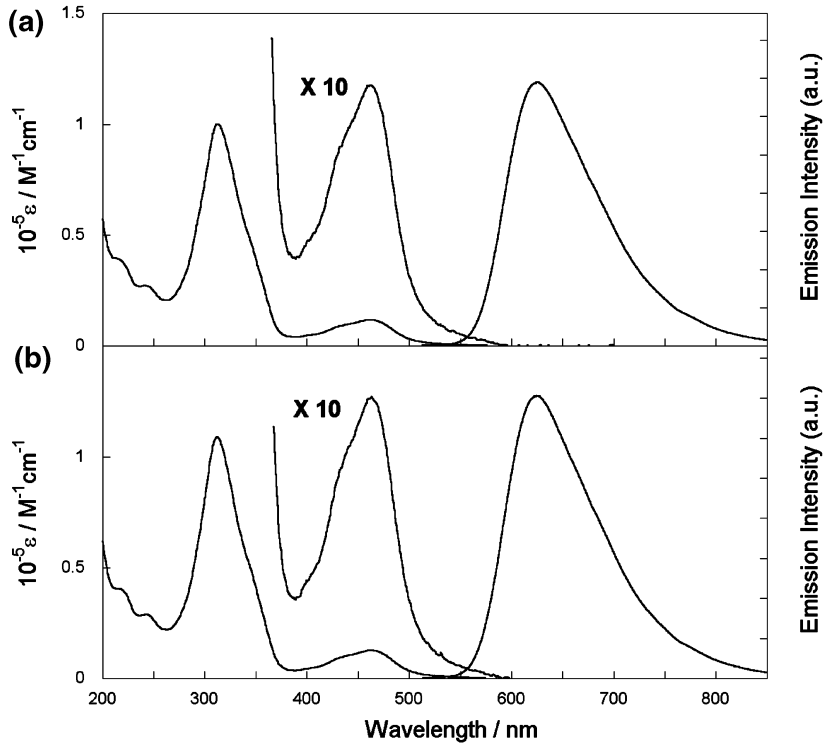

Figure 4. Absorption and emission spectra for $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ in CH_3CN at room temperature: (a) fac complex and (b) mer complex.

result of the strong adsorption on the working electrode because they have amide protons in the ligands.

To discuss the photophysical properties of the *fac*/*mer*-ruthenium(II) complexes, the energy levels for MLCT excited states, as well as those for the ground states, are required. As already discussed in the literature,[38] the relative ground-state energies are approximated by comparison of the $Ru^{2+/3+}$ potentials for the ruthenium complexes to that for $[Ru(bpy)_3]^{2+}$. The energy placement of the ^{3}MLCT state relative to the ground state would be obtained by adding the emission energy to the relative ground-state energy. Unexpectedly, almost no difference between the fac (0.960 V) and mer (0.962 V) complexes was observed in the oxidation potentials (Figure 3b). That is, they indicate that the energy level for the ground state of *fac*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ is approximately similar to that for the mer complex.

Photophysical Properties. The absorption and emission spectra for *fac/mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ in acetonitrile at room temperature (293 ± 0.5 K) are shown in Figure 4. The obtained photophysical properties are listed in Table 1. The maximum wavelengths (λ_{max}) for the MLCT bands in the absorption spectra in acetonitrile are 463 nm for both *fac*- and *mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$. When the fac and mer complexes were excited at that wavelength, they showed emission spectra with maximum emission wavelengths (λ_{em}) at 626 and 625 nm, respectively. The emission quantum yields (Φ) and lifetimes (τ) at room temperature were 0.094 and 1.50 μs, respectively, for the fac complex and 0.098 and 1.51 μs, respectively, for the mer complex. The photophysical properties for both *fac*- and *mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH(c\text{Hex}))_3]^{2+}$, in which cyclohexyl amide groups were introduced at the C termini, were almost the same as those for $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$. *fac/mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}N(c\text{Hex})_2)_3]^{2+}$ showed absorption and emission spectra with slightly shorter maximal wavelengths than $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH(^t\text{Bu (or } c\text{Hex}))_3]^{2+}$. However, for all complexes in this work, no significant difference between the fac and mer isomers was observed in absorption and emission spectra in acetonitrile at room temperature. This is similar to the reports by Fletcher et al., describing the photophysical properties of the *fac*/*mer*-ruthenium(II) tris-chelate complexes of 2,2′-bipyridine-5-carboxylic acid methyl ester.[14,15]

Table 1. Photophysical Properties of $[Ru(L)_3](PF_6)_2$ in CH_3CN at Room Temperature

		absorption		emission		
ligand		λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{em} (nm)	τ (μs)	Φ
MeCO-**5Bpy**-NH^{t}Bu	fac	463	1.18×10^4	626	1.49_8	0.094
	mer	463	1.27×10^4	625	1.50_6	0.098
MeCO-**5Bpy**-NH(*c*Hex)	fac	463	1.19×10^4	625	1.62_3	0.100
	mer	463	1.29×10^4	624	1.37_5	0.094
MeCO-**5Bpy**-N(*c*Hex)$_2$	fac	451	1.20×10^4	613	1.46_1	0.096
	mer	451	1.29×10^4	610	1.85_4	0.123

We have already found that the photophysical properties of ruthenium(II) complexes with the symmetrical bipyridyl ligands bearing amide groups at the 5,5′-positions are quite different depending on the orientation of the amide groups, −CONHR or −NHCOR.[12] In this work, the maximum wavelengths in the absorption and emission spectra for the ruthenium(II) complexes of the unnatural amino acid derivatives, which possessed both −CONHR and −NHCOR

(38) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227−234.

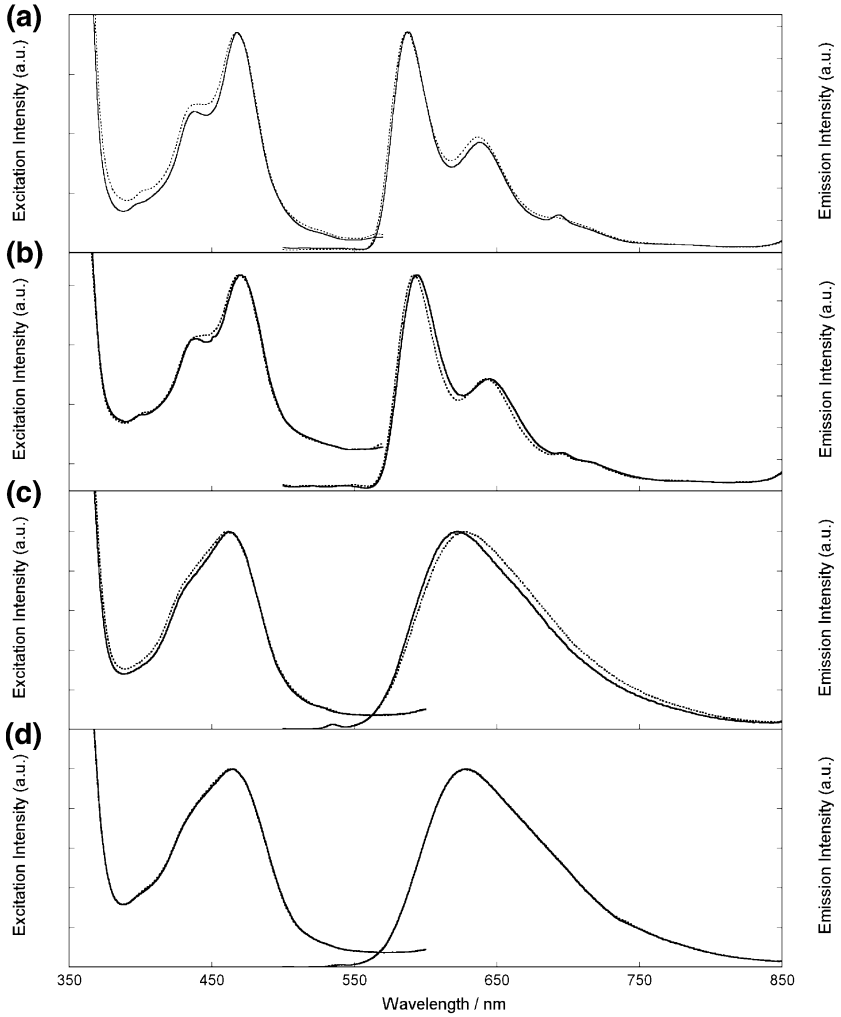

Figure 5. Emission and excitation spectra for the fac isomer (solid line) and the mer isomer (broken line) of $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$: (a) in EPA at 77 K ($\lambda_{ex}$ = 463 nm), (b) in EtOH/MeOH (4:1 (v/v)) at 77 K (λ_{ex} = 463 nm), (c) in EPA at room temperature (λ_{ex} = 463 nm), and (d) in EtOH/MeOH (4:1 (v/v)) at room temperature (λ_{ex} = 463 nm).

groups, were found to be approximately intermediate between the ruthenium(II) complexes with RNHCObpy and RCONHbpy. On the other hand, quite high quantum yields and long lifetimes in the emission were observed for the ruthenium(II) complexes with unnatural amino acid derivatives. This tendency is similar to that for $[Ru(5RCONHbpy)_3]^{2+}$ but not that for $[Ru(5RNHCObpy)_3]^{2+}$.

The emission and excitation spectra for the ruthenium(II) complexes with the unnatural amino acid derivatives were measured in typical glassy solutions, EPA (5:5:2 diethyl ether/isopentane/ethanol (v/v/v)) and EtOH/MeOH (4:1 (v/v)), at 77 K under Ar (Figure 5 and Table 2). In EPA at 77 K, the maximum wavelengths in the emission spectra are 587 nm for both the fac and mer complexes of $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ (Figure 5a). No significant difference between the fac (468 nm) and mer (467 nm) complexes was observed at the MLCT bands in the excitation spectra. In EtOH/MeOH (4:1 (v/v)) at 77 K, the maximum wavelengths in the emission spectra for the fac and mer complexes were 594 and 592 nm, respectively, showing no significant difference, although they were slightly longer than those in EPA (Figure 5b). Thus, the emission and excitation spectra in EPA and EtOH/MeOH (4:1 (v/v)) at 77 K did not show a significant difference between the two isomers, as well as those in acetonitrile at room temperature. On the basis of the results showing no difference between the emission wavelengths of the fac and mer complexes at 77 K and the cyclic voltammetric studies which revealed that the energy levels of the ground states for the two isomers were equivalent, the energy level of the ^{3}MLCT excited state for the fac complex was found to be almost the same as that for the mer complex.

Table 2. Maximum Wavelengths (λ_{em}) and the Half-Band Widths ($\Delta\lambda_{1/2}$) in Emission and Excitation Maximum Wavelengths (λ_{ex}) of *fac/mer*-$[Ru(MeCO\text{-}5Bpy\text{-}NH^tBu)_3]^{2+}$ in EPA and EtOH/MeOH (4:1 (v/v)) at 77 K and Room Temperature under Ar

		77 K		room temperature		
isomer	solvent	λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\lambda_{1/2}$ (nm)
fac	EPA[a]	468	587	462	622	101
	EM[b]	469	594	465	628	105
mer	EPA[a]	467	587	461	628	106
	EM[b]	469	592	464	628	105

[a] EPA = diethyl ether/isopentane/ethanol (5:5:2 (v/v/v)). [b] EM = EtOH/MeOH (4:1 (v/v)).

To examine solvent effects, the emission and excitation spectra were then measured in EPA and EtOH/MeOH (4:1

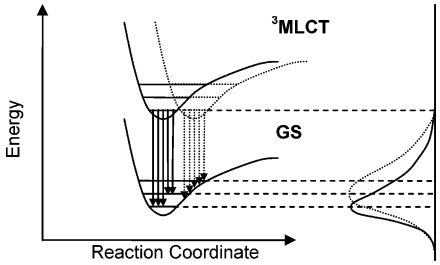

Figure 6. Energy profiles for the fac isomer (solid line) and the mer isomer (broken line) of $[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ in EPA at room temperature.

(v/v)) at room temperature (Figure 5c and d). Although the excitation spectra for *fac*- and *mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^t\text{-}Bu)_3]^{2+}$ in EPA showed almost the same maximum wavelengths (fac, 462 nm; mer, 461 nm) at the MLCT bands, the maximum wavelength in the emission spectrum of the fac complex was 622 nm, whereas that for the mer complex was 628 nm, which was slightly longer than that for the fac complex. However, in EtOH/MeOH (4:1 (v/v)) at room temperature, the maximum wavelengths in the emission spectra for the fac and mer isomers were both 628 nm, which is identical to that for the mer complex in EPA at room temperature.

The electronic states and the solvated structures of the ruthenium(II) complexes with unnatural amino acid derivatives would be affected by protic polar solvents, such as ethanol and methanol, because the amide groups in their ligands in the complexes could interact with the protic solvents, probably through hydrogen bondings or electrostatic interaction. To investigate the solvent effects in detail, the degrees of broadening of the emission bands for the fac and mer complexes in EPA and EtOH/MeOH (4:1 (v/v)) were estimated based on the half bandwidth ($\Delta\lambda_{1/2}$, nm) (Table 2). The half bandwidth for the mer complex in EPA was not different from that in EtOH/MeOH (4:1 (v/v)). On the other hand, the emission spectrum for the fac complex in EPA was sharper than that in EtOH/MeOH (4:1 (v/v)). The results, as well as the peak shift depending on the solvents, may be elucidated as the difference in the reaction coordinates in the ^{3}MLCT excited states between the two isomers, as shown in Figure 6. The molecular structures in the ^{3}MLCT states should change from those of the ground state (GS). In the cases of the ruthenium complexes with unnatural amino acid derivatives in alcoholic solutions, the changes could depend on the solvation modes. As shown in Figure 6, a small difference in the structures between the ^{3}MLCT and GS shows a sharp emission band, whereas a larger difference makes the emission band broader. As shown in Table 2, almost no difference in the emission maximum wavelengths for the mer complex was observed between that in EPA and that in EtOH/MeOH (4:1 (v/v)). On the other hand, the emission maximum wavelength for the fac complex in EPA becomes shorter than that in EtOH/MeOH (4:1 (v/v)). In EtOH/MeOH (4:1 (v/v)), both the fac and mer complexes are considered to fully interact with the protic solvents: the amide groups may interact through hydrogen bonding or electrostatic interaction. Even in EPA, in which the alcohol content is much less than in EtOH/MeOH (4:1

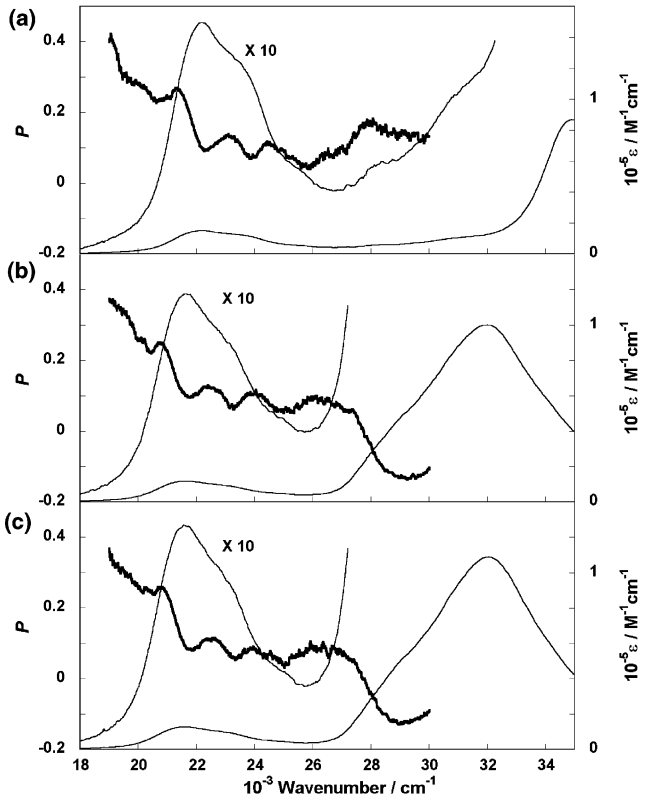

Figure 7. Absorption spectra in CH_3CN at room temperature and excitation polarization spectra in EtOH/MeOH (4:1 (v/v)) at 77 K: (a) $[Ru(bpy)_3]^{2+}$ (λ_{em} = 579 nm), (b) *fac*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ (λ_{em} = 594 nm), and (c) *mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ (λ_{em} = 592 nm).

(v/v)), the mer complex still interacts with the protic solvents. However, the fac complex might not be able to interact with alcohol in EPA but can interact in EtOH/MeOH (4:1 v/v)). These results imply that the mer complex interacts more strongly with the protic polar solvents than the fac complex.

Excitation Polarization. Excitation polarization spectra for *fac*/*mer*-$[Ru(MeCO\text{-}\mathbf{5Bpy}\text{-}NH^tBu)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ were measured at 19 000−30 000 cm^{-1} in EtOH/MeOH (4:1 (v/v)) glassy solutions at 77 K under Ar. For comparison, the ruthenium(II) tris-chelate complexes with 5^{t}BuNHCObpy and 5MeCONHbpy as the symmetrical bipyridyl ligands were measured in EPA, but otherwise the same conditions were used. The degrees of polarization were estimated as *P* values, described in detail in the Experimental Section. The spectra at the higher-energy region (>30 000 cm^{-1}) could not be measured because the polarizer showed absorption in this region. The experimental error in the *P* values was within ±0.02, and the excitation polarization spectra exhibited good reproducibility.

The *P* values at the MLCT band for $[Ru(bpy)_3]^{2+}$ in the excitation polarization spectrum, as shown in Figure 7a, are ca. +0.14 at 23 000−26 000 cm^{-1} and ca. +0.28 at 21 300 cm^{-1}, which are consistent with the previously reported values.[21,26] The *P* values in the excitation polarization spectrum for $[Ru(bpy)_3]^{2+}$ have so far been discussed in the literature.[21−30] Fujita and Kobayashi discussed the limiting *P* values for $[Ru(bpy)_3]^{2+}$ by considering the combination of absorption and emission oscillators.[21] In the report, they

assumed that $[Ru(bpy)_3]^{2+}$ had D_3symmetry even in the excited state. Because the absorption oscillator in the MLCT region (21 000−26 000 cm^{-1}) for $[Ru(bpy)_3]^{2+}$ was dominant perpendicular to the C_3 axis,[22,39] the theoretical limiting P values had been expected to be $+1/7$ and $-1/3$ when the emission involved the planar (x, y) and linear (z) emission oscillators, respectively. Although their interpretation could explain the P values at the higher region (> 23 000 cm^{-1}) in the MLCT band, this could not account for the P value at 21 300 cm^{-1}, which was over $+1/7$. To elucidate the P value, many studies have been performed.[21,22,24−30] DeArmond and co-workers indicated that the peak at 21 300 cm^{-1} in the excitation polarization spectrum for $[Ru(bpy)_3]^{2+}$ was based on the lowest-excited state, in which the excited electron is localized in a bipyridyl chromophore, $[(bpy)_2Ru^{III}(bpy)]^{2+}$.[30] They concluded that the absorption and emission oscillators for the lowest-excited state, which were oriented parallel along the CT transition from the central metal to the one localized bipyridine, were both linear, giving a P value greater than $+1/7$. Furthermore, they described that the lowest-excited state for $[Ru(bpy)_3]^{2+}$ should have a lower symmetry, such as C_2 or C_{2v}, than D_3, which Fujita et al. had assumed. The localized excited state for $[Ru(bpy)_3]^{2+}$ was supported by the time-resolved resonance Raman studies,[40,41] the solvent dependence studies for the MLCT transitions,[42] and the temperature-dependent ESR studies.[43,44]

The excitation polarization spectra for *fac/mer*-[Ru(MeCO-**5Bpy**-NH^{t}Bu)$_3$]$^{2+}$, monitored at emission maximum wavelengths (fac, 594 nm; mer, 592 nm) in EtOH/MeOH (4:1 (v/v)) at 77 K, are shown in Figure 7b and c, respectively, with the absorption spectra in acetonitrile at room temperature. The P values in the MLCT region for both isomers are ca. +0.13 at 23 000−25 000 cm^{-1} and ca. +0.26 at 20 700 cm^{-1}, which correspond to $+1/7$ and over, respectively. The negative P values, ca. −0.13, are observed at > 28 000 cm^{-1} in the $\pi-\pi^*$ region, where the measurements for the fac/mer complexes are possibly contrary to those for $[Ru(bpy)_3]^{2+}$ because the $\pi-\pi^*$ absorption bands of the fac/mer complexes in this study are red-shifted and avoid the region in which the polarizer has absorption. It is noteworthy that almost no difference between the fac and mer isomers is observed in the excitation polarization spectra. Furthermore, they are very similar to the spectrum for $[Ru(bpy)_3]^{2+}$. The spectra for the ruthenium(II) tris-chelate complexes with the symmetrical bipyridyl ligands, 5^{t}BuNHCObpy and 5MeCONHbpy, also exhibit similar P values, as shown in Figure 8, although large shifts in the wavelengths, which correspond to the shifts in the absorption spectra, are observed.

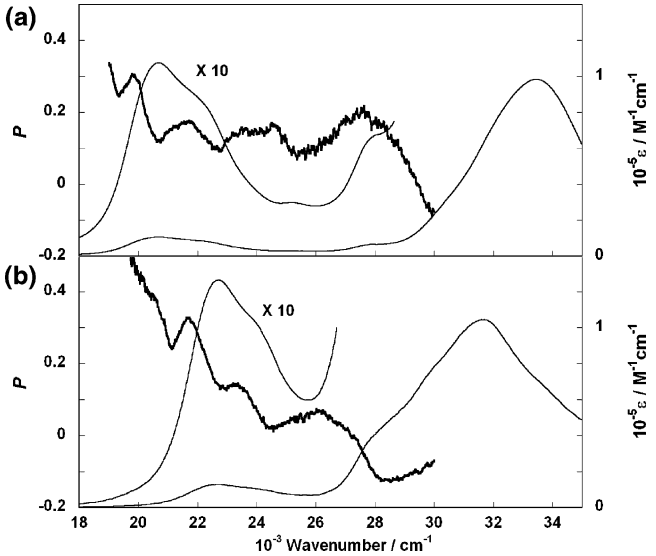

Figure 8. Absorption spectra in CH_3CN at room temperature and excitation polarization spectra in EPA at 77 K: (a) $[Ru(5^tBuNHCObpy)_3]^{2+}$ (λ_{em} = 619 nm) and (b) $[Ru(5MeCONHbpy)_3]^{2+}$ (λ_{em} = 568 nm).

To consider the similarity of the excitation polarization spectra between the fac and mer isomers, of which the symmetries at the ground states are different, we start the discussion based on the assignments of the P values, reflecting the relationships between the absorption and the emission oscillators. The peaks at 20 700 cm^{-1} in the excitation polarization spectra for the fac/mer isomers are assigned to the lowest-excited states, in which the excited electron is localized to one bipyridyl ligand, as well as in the case of $[Ru(bpy)_3]^{2+}$ (21 300 cm^{-1}). Therefore, the transitions in absorption for the fac/mer complexes occur, as well as in $[Ru(bpy)_3]^{2+}$, from the central metal to the localized bipyridyl π^* MO, and the transitions in emission are the reverse. In these cases, the absorption and emission oscillators for both the isomers are linear; it is known that the combination of the linear absorption and the linear emission oscillators gives a P value of over $+1/7$.[30] The higher-energy region (22 000−25 000 cm^{-1}) in the MLCT band for the fac/mer complexes corresponds to the region (23 000−26 000 cm^{-1}) for $[Ru(bpy)_3]^{2+}$. In this region, the absorption and emission oscillators for $[Ru(bpy)_3]^{2+}$ are planar (x, y) because of the transition to the E state, giving a P value of $+1/7$.[21] On the other hand, the mer complex does not have a transition to the E state because its symmetry is C_1. The fac complex with C_3 symmetry also may not have a transition to the E state in this region. However, the P values for the fac/mer complexes would give $+1/7$, as for $[Ru(bpy)_3]^{2+}$ (D_3 symmetry). These findings suggest that the transitions in the MLCT regions for these isomers occur from the central metal to the bipyridyl ligands, and therefore, the absorption and emission oscillators in these isomers would be relatively oriented on a plane perpendicular (x, y) to the C_3 axis of the parent ruthenium(II) tris(2,2′-bipyridine) complex.

It was originally expected that the absorption and emission oscillators for the fac/mer complexes were affected by the dipole moments along the long axis in the unsymmetrical ligands because the spin-forbidden transitions would borrow

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the intense $\pi-\pi^*$ transition in the ligand. However, there was actually no difference in the *P* values among the fac and mer isomers and $[Ru(bpy)_3]^{2+}$. This suggests that the orientations of the absorption and emission oscillators, in the case of the ruthenium(II) tris-chelate complexes with the π-conjugated bidentate ligands, such as 2,2′-bipyridine, would not be affected by the symmetries of the complexes. It is also surmised that the *P* values for the derivatives would be similar to that for $[Ru(bpy)_3]^{2+}$, although the peak shifts in the spectra could be observed.

The lowest-excited state for the fac complex has only one localized structure because the three ligands in the complex are equivalent because of the C_3 symmetry at the ground state. On the other hand, the lowest-excited state for the mer complex has three different localized structures because the three ligands are unequivalent because of the C_1 symmetry at the ground state. Therefore, the energy of the lowest-excited state for the fac complex would be different than that for the mer complex. However, the detected peak based on the lowest-excited state for the fac complex is detected at almost the same point as that for the mer complex, and furthermore, these peaks are similar to that for $[Ru(bpy)_3]^{2+}$. These results suggest that the energy levels of the three different localized structures for the mer complex, in which they are degenerated or thermal equilibrium is reached even at 77 K because of the small energy difference, are very close to that for the fac complex. From these results, we would expect that we could not observe a difference in the *P* values but in the wavenumbers of peaks in the excitation polarization spectra between the fac and mer complexes, if we could obtain these isomers with different energies even at the ground states. One strategy suggested is to introduce a much more electron-donating or -accepting substituent to the bipyridyl ligand at the 5-position rather than to the group at the 5′-position. The increase in the unsymmetry would possibly cause the energies of the fac and mer complexes to differ. Another strategy is to design the ligands so that they interact with other ligands in the complex. Such a design would also allow the difference in the energies between the fac and mer complexes to become larger.

In conclusion, we have, for the first time, measured the excitation polarization spectra for the fac and mer isomers of the ruthenium(II) tris-chelate complexes with the unsymmetrical bipyridyl ligands. No difference in the spectra between the fac and mer complexes has been observed, and they have also been similar to that for $[Ru(bpy)_3]^{2+}$. Moreover, the ruthenium(II) tris-chelate complexes with 5^t-BuNHCObpy and 5MeCONHbpy have shown similar *P* values in the MLCT bands, although shifts in the peaks in the excitation polarization spectra have been observed. The reasons that the spectra have been similar among these complexes have been discussed in detail. The discussion suggests that the excitation polarization spectra in the case of the ruthenium(II) tris(2,2′-bipyridine)-type complexes would be similar to that for $[Ru(bpy)_3]^{2+}$, independent of the symmetries of the complexes and the types of the bipyridyl ligands, even though shifts in the peaks in the excitation polarization, as well as in the absorption spectra, could be observed.

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Supporting Information Available: Ratio of *fac*/*mer*-ruthenium complexes in syntheses, HPLC charts for the fac and mer complexes, ^{1}H and ^{13}C NMR, IR, and MS spectra for the ligands, and ^{1}H and ^{13}C NMR spectra for the ruthenium complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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