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Synthesis, photochemistry, and electrochemistry of ruthenium(II) polypyridyl complexes anchored by dicobalt carbonyl units

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Abstract

A novel hybrid complex system of ruthenium polypyridyl complexes anchored by dicobalt carbonyl units, $[Ru(bpy)_2\{phen–C\{Co_2(CO)_4(dppm)\}C–tolyl\}](PF_6)_2$ (**1**) and $[Ru(bpy)_2\{tolyl–C\{Co_2(CO)_4(dppm)\}C–phen–C\{Co_2(CO)_4(dppm)\}C–tolyl\}](PF_6)_2$ (**2**), has been prepared from the dicobalt carbonyl complex $Co_2(CO)_6(dppm)$ (dppm = bis(diphenylphosphino)methane) and the ruthenium complex $[Ru(bpy)_2(phen–\equiv–tolyl)](PF_6)_2$ (**3**) or $[Ru(bpy)_2(tolyl–\equiv–phen–\equiv–tolyl)](PF_6)_2$ (**4**).

The present Ru–Co$_2$ hybrid complexes **1** and **2** are nonluminescent at room temperature, although precursor ruthenium polypyridyl complexes, such as **3** and **4**, clearly show phosphorescence from the ^{3}MLCT excited state. The emission quenching of these hybrid complexes indicates the intramolecular energy transfer from the ruthenium polypyridyl unit to the dicobalt carbonyl unit(s) and then to the ground state by a radiationless deactivation process accompanied by a vibrational relaxation of the dicobalt carbonyl unit(s). This interpretation is supported by spectral change measurements along with constant potential electrolysis and electrochemical data.
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1. Introduction

Growing interest has focused on the useful properties and applications of dicobalt carbonyl derivatives to organometallic chemistry as metallodendrimers [1–3] and to synthetic chemistry for developing the Pauson–Khand reaction [4–7]. Recent studies on heteronuclear metal complexes and clusters containing dicobalt carbonyl organometallics, M–Co$_2$ (M = Pd, Ru, Fe, Co, etc.), are particularly intriguing not only because of their unique structures but also because of their potential use as catalysts [8–12]. To the best of our knowledge, however, the photophysical characteristics of these M–Co$_2$ complexes and clusters have not been well explored, although electro-

chemical studies have been done on several of these complexes [11–14].

On the other hand, in recent decades a tremendous number of ruthenium polypyridyl complexes have been subjected to extensive photophysical and electrochemical examinations, and an understanding of their electronic excited states has developed. For example, several manganese complexes linked by a ruthenium polypyridyl framework have been studied as models of artificial photosynthesis [15]. These combined systems have exhibited emission quenching by an intramolecular energy transfer from the ruthenium polypyridyl unit to the manganese moiety under many circumstances. Recently, ruthenium polypyridyl complexes containing a bipyridine or phenanthroline ligand with ethynylarene substituents, Ru-(bpy)$_2$(L)$^{2+}$ (L = ethynylarene-bipyridine or phenanthroline) have been synthesized, and potential applications of

these complexes to opt-electronic materials have been clarified [16–18]. This type of ruthenium complex is a good candidate for the construction of a hybrid system with the dicobalt carbonyl derivatives mentioned above.

Thus, we decided to synthesize ruthenium polypyridyl complexes anchored by dicobalt carbonyl unit(s) on ethynylarene substituents. In the present paper, we report the synthesis, photophysical properties, and electrochemistry of Ru–Co$_2$ hybrid complexes constructed from a Werner type of ruthenium polypyridyl unit and an organometallic type of dicobalt carbonyl unit(s); these units are connected to each other by phenanthrolines as a π-conjugated ligand. The newly formed hybrid complex systems are [Ru(bpy)$_2$\{phen–C\{Co$_2$(CO)$_4$(dppm)\}C–tolyl\}](PF$_6$)$_2$ (**1**) and [Ru(bpy)$_2$\{tolyl–C\{Co$_2$(CO)$_4$(dppm)\}C–phen–C\{Co$_2$-(CO)$_4$(dppm)\}C–tolyl\}](PF$_6$)$_2$ (**2**), as shown in Chart 1. Interestingly, these Ru–Co$_2$ complexes exhibit obvious emission quenching from the ruthenium polypyridyl unit as well as emission recovery accompanied by constant potential electrolysis. These results are interpreted in terms of the intramolecular energy transfer from the ruthenium polypyridyl unit to the dicobalt carbonyl unit(s) on the basis of the photophysical and electrochemical data for these Ru–Co$_2$ hybrid complexes.

2. Results and discussion

2.1. Synthesis and characterization

The precursor ruthenium complexes [Ru(bpy)$_2$(phen–$\equiv$–tolyl)](PF$_6$)$_2$ (**3**) and [Ru(bpy)$_2$(tolyl–$\equiv$–phen–$\equiv$–tolyl)](PF$_6$)$_2$ (**4**) were prepared in good yields by a method similar to that described in our recent report [19]. The ligand 3-(4-tolylethynyl)-phenanthroline, phen–$\equiv$–tolyl, or 3,8-bis(4-tolylethynyl)-phenanthroline, tolyl–$\equiv$–phen–$\equiv$–tolyl, and Ru(bpy)$_2$Cl$_2$ were refluxed in ethanol for 5 h. After filtration of the reaction mixture, the filtrate was concentrated and added to water containing NH$_4$PF$_6$. Orange precipitates **3** and **4** were collected by filtration. The Ru–Co$_2$ heteronuclear hybrid complexes, [Ru(bpy)$_2$-\{phen–C\{Co$_2$(CO)$_4$(dppm)\}C–tolyl\}](PF$_6$)$_2$ (**1**) and [Ru(bpy)$_2$\{tolyl–C\{Co$_2$(CO)$_4$(dppm)\}C–phen–C\{Co$_2$(CO)$_4$-(dppm)\}C–tolyl\}](PF$_6$)$_2$ (**2**), were synthesized from ruthenium complex **3** or **4** and Co$_2$(CO)$_6$(dppm) (dppm = bis(diphenylphsphino)methane) and were obtained in good yields. Novel Ru–Co$_2$ complexes **1** and **2** were characterized by IR, UV–Vis, ESI-mass spectroscopies, and elemental analysis.

We first attempted to synthesize Ru–Co$_2$ hybrid complexes by using Co$_2$(CO)$_8$ instead of Co$_2$(CO)$_6$(dppm) and **3** or **4**. The reaction proceeded smoothly at room temperature, but we did not obtain analytically pure samples. Presumably some decomposed impurities could not be removed by our extraction and crystallization method. A recent study on Co$_2$(alkyne)(CO)$_6$ complexes showed that the photochemical CO loss is easily induced under visible light [20]. We surmise that CO loss may likewise occur during purification.

The IR spectra of Ru–Co$_2$ hybrid complexes **1** and **2** show three strong v(C$\equiv$O) bands (2025s, 1996vs, 1970vs cm^{-1}), which are typical for this type of compound, Co$_2$(alkyne)(CO)$_4$(dppm) [21]. Additionally, Ru–Co$_2$ hybrid complexes lack the v(C$\equiv$C) band, while the precursor ruthenium complexes **3** and **4** exhibit the v(C$\equiv$C) stretches at 2219 cm^{-1} for **3** and 2213 cm^{-1} for **4**. These data clearly indicate the formation of the [Co$_2$(alkyne)-
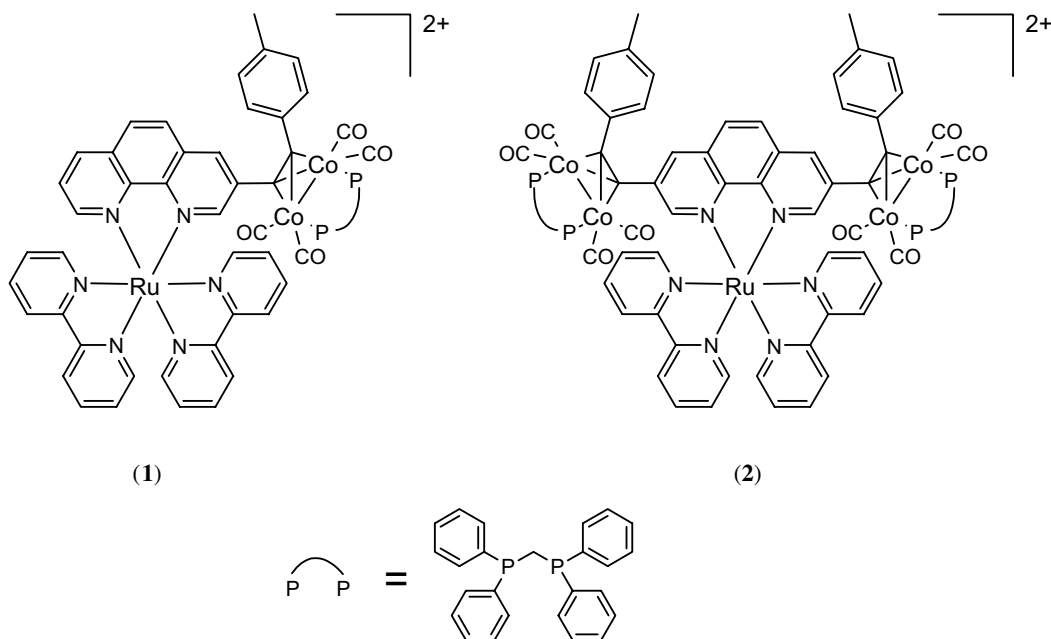

(**1**)   (**2**)

Chart 1.

(CO)$_4$(dppm)]-type unit(s) in **1** and **2**. The existence of the Co$_2$(CO)$_4$(dppm) unit in Ru–Co$_2$ hybrid complexes is further supported by the ESI-mass spectra.

The ESI-mass spectrum of **1** contained the molecular ion [Ru(bpy)$_2$\{phen–C\{Co$_2$(CO)$_4$(dppm)\}C–tolyl\}]$^{2+}$ at *m/z* 661, with a satisfactory isotopic matching to the simulated pattern. The ESI-mass of **2** was more indicative of two isotopic envelopes. One envelope, centered at *m/z* 1025, was assigned to [Ru(bpy)$_2$\{tolyl–C\{Co$_2$(CO)$_4$-(dppm)\}C–phen–C\{Co$_2$(CO)$_4$(dppm)\}C–tolyl\}]$^{2+}$ (M^{2+}), and the other, at *m/z* 715, was assigned to [M–Co$_2$(CO)$_4$-(dppm)]$^{2+}$. The isotopic signals in these two envelopes of **2** are consistent with the simulated patterns of the respective estimated cations.

2.2. Photophysical properties

Table 1 culls the numerical data from the UV–Vis and emission spectra for **1–4**. The UV–Vis absorption spectrum of precursor complex **3**, which contains a tolylethynyl substituent attached to the phenanthroline, exhibits a distinct absorption peak assignable to the π–π∗(C≡C) absorption (maximum at 346 nm) in the 300–400 nm region and a typical absorption band of ruthenium polypyridyl complexes assignable to the dπ(Ru)–π (phen) MLCT absorption in the 400–500 nm region (Fig. 1). On the other hand, the novel Ru–Co$_2$ complex **1** does not exhibit a distinct π–π∗(C≡C) absorption in the 300–400 nm region, while the MLCT absorption band is intact except for the increase in absorption intensity. Fig. 2 shows a quite similar spectral difference between **2** and **4**. The absorption spectrum of **2** clearly lacks the π–π∗(C≡C) band, while the intensive π–π∗ absorption is observed for **4** in the 300–400 nm region. The absence of π–π∗ absorption is due to the formation of the alkyne–Co$_2$(CO)$_4$(dppm) skeletons on the triple bond of the substituted phenanthroline ligand; the lack of the ν(C≡C) band in the IR spectrum discussed above supports this interpretation. Furthermore, the absorbance in the 300–500 nm region for **2** is larger than that for **4** except that the π–π∗(C≡C) absorption band mentioned above and the gain in the absorbance from **4** to **2** are both more conspicuous when this pair is compared with those of **1** and **3**. This distinct increase should be attributable to overlapping of MLCT and MMCT absorptions originated from the dicobalt carbonyl units of Ru–Co$_2$ complexes in this region, because **2** has two Co$_2$(CO)$_4$(dppm) units and thus
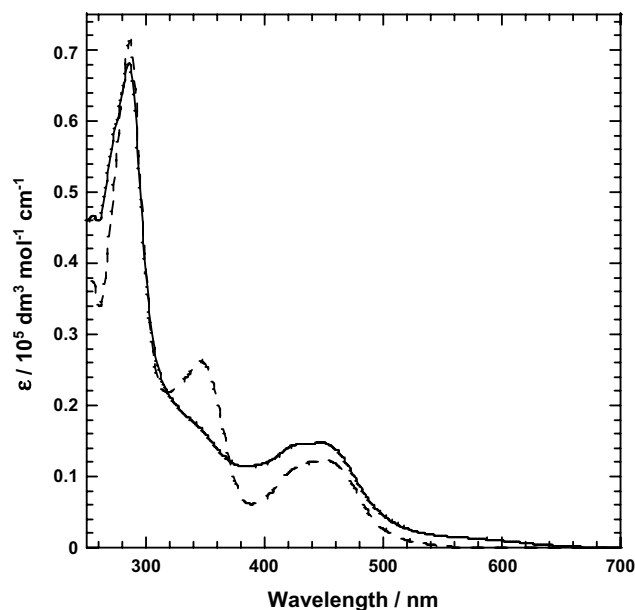

Fig. 1. UV–Vis absorption spectra of **1** (—) and **3** (---) in CH$_3$CN solution at room temperature.
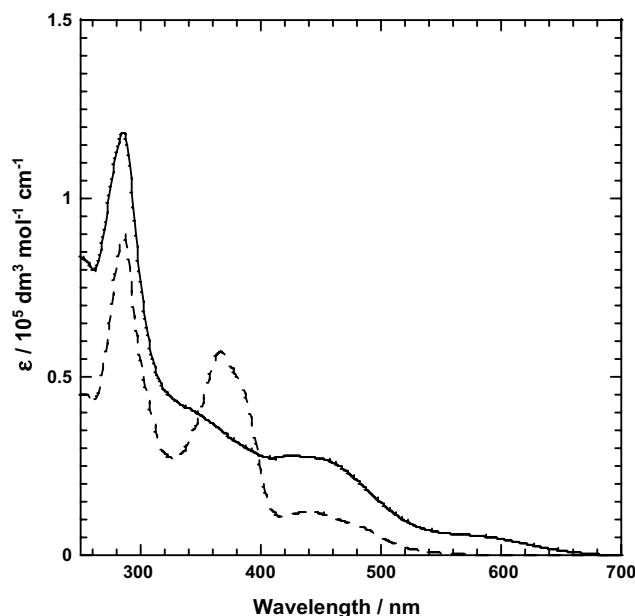

Fig. 2. UV–Vis absorption spectra of **2** (—) and **4** (---) in CH$_3$CN solution at room temperature.

Table 1
Relevant photophysical data for compounds **1–4**[a]

Compound	UV–Vis absorption λ_{abs} (nm) (ε, 10^4 dm^3 mol^{-1} cm^{-1})	Emission λ_{em} (nm)
1	585 (0.13), 451 (1.5), 428 (1.5), 286 (6.8)	
2	585 (0.53), 455 (2.7), 423 (2.8), 286 (11.8)	
3	451 (1.2), 425 (1.1), 346 (2.6), 286 (7.1)	635
4	480 (0.9), 439 (1.2), 384 (4.8), 367 (5.7), 286 (9.0)	661

[a] UV–Vis and emission spectra were measured in an acetonitrile solution at room temperature.

the absorbance in this region should gain more intensity than **1** [22]. In addition, the spectrum of **2** has a broad band at approximately 585 nm with a tail to the 650–700 nm area, while the broad band of **1** shows a weak absorption at approximately 585 nm with a tail to the 600–650 nm area. These bands should be assigned to the d–d transition; this assignment is supported by a previous experimental and theoretical study on $[Co_2(CO)_4(dppm)]_2$–diyne complexes [22].

Luminescence spectra of the precursor complexes **3** and **4** were observed as emissions around 650 nm in CH_3CN solution at room temperature. This type of luminescence is typical as phosphorescence from the $d\pi(Ru)$–π (diimine) ^{3}MLCT excited state, which has been reported in many ruthenium polypyridyl complexes [23]. Interestingly, such a phosphorescent band has hardly been detected for Ru–Co_2 complexes **1** and **2** by our commercial emission spectrophotometer. To the best of our knowledge, this kind of behavior has not previously been reported for heteronuclear metal complexes linked with dicobalt carbonyl units, although emission quenching has been reported for a few examples of fluorescent organic compounds, including dicobalt carbonyl complex [24]. The emission quenching for Ru–Co_2 hybrid complexes indicates that the photoexcited state of this Ru–Co_2 system is susceptible to efficient intramolecular energy transfer from the ruthenium polypyridyl unit to the dicobalt carbonyl unit and then leads to the ground state by a radiationless deactivation accompanied by a vibrational relaxation of the dicobalt carbonyl unit. Furthermore, we measured the emission spectral change of precursors **3** and **4** by adding the $Co_2(CO)_6(dppm)$ complex by an amount that was more than 20-fold the amount of each precursor complex, but we found no emission spectral change. This control experiment clearly indicates that $Co_2(CO)_6(dppm)$ is not responsible for emission quenching via the intermolecular energy transfer mechanism.

2.3. Electrochemical study

Table 2 culls the electrochemical data from voltammograms obtained by cyclic voltammetry (CV) and osteryoung square wave voltammetry (OSWV) for complexes **1**–**4**. The cyclic voltammograms for all of the complexes show behavior typical of ruthenium polypyridyl complexes. The anodic peaks corresponding to the oxidation of the ruthenium(II) center of each of these complexes were observed at around 1.3 V although the redox peaks for complexes **1** and **2** were observed as irreversible peaks even at 4.9 V s^{-1} scan rate; The $E_{1/2}(Ru^{3+/2+})$ were obtained at 1.29 V for **3** and 1.32 V for **4**. Products formed after the oxidation process of dicobalt carbonyl unit(s) discussed below may be involved in the irreversibility of the redox peak, which belongs to $Ru^{3+/2+}$ on **1** and **2**.

One additional reversible oxidation peak potential was observed at 0.70 and 0.71 V, respectively, for **1** and **2** by CV at 4.9 V s^{-1} scan rate and OSWV; each of these peaks was assigned to the oxidation of the dicobalt carbonyl unit(s). The counterpart reduction peaks of the oxidation of the dicobalt carbonyl unit(s) were only observed by faster scanning than 0.9 V s^{-1} scan rate and this observation for **1** and **2** was assumed to be due to occur a so-called EC reaction after the oxidation of the dicobalt unit. The EC reaction on the dicobalt carbonyl unit(s) is further supported by the electrolysis experiment described in the following section. The lower $E_{1/2}(Co^{1+/0})$ potential of the dicobalt units, compared to $E_{1/2}(Ru^{2+/3+})$ of the ruthenium units, should be the driving force behind the intramolecular energy transfer for Ru–Co_2 complexes under the photoexcited state. The redox process of two cobalt units in **2** is observed as almost one redox peak even at 10.0 V s^{-1} scan rate, although **2** has two cobalt carbonyl units in the substituted phenanthroline. This result is attributable to the little electric communication between the two cobalt units and the small difference between two oxidation potentials for the two cobalt units. This interpretation is supported by the previous study on $[Co_2(CO)_4(dppm)]_2$–diyne complexes bridged with some aromatic rings [25].

The first cathodic peaks of complexes **1**–**4** are observed in a wide potential range between −1.0 and −1.4 V, while the second peaks are observed at around −1.5 V, as shown in Table 2. The first peaks are assigned to the reduction of the substituted phenanthroline ligand, and the second ones to that of one of the bipyridine ligands in each complex. We made these assignments for the following reasons. First, previous data suggest that the reduction potential due to the cobalt in dicobalt carbonyl units should be more negative than −1.6 V [11,22,25]. Second, the reduction potential $E_{1/2}$ around −1.5 V for **1**–**4** are close to the second reduction potentials ($E_{1/2} = -1.55$ V) of Ru(bpy)$_3$(PF$_6$)$_2$, which were assigned as the second reduction of bipyridine ligands under similar experimental conditions [26].

2.4. Spectral change under electrolysis

Ru–Co_2 compound **1** was subjected to measurements of both the emission and UV–Vis spectral changes under the constant potential electrolysis (potential at 0.98 V vs.

Table 2
Electrochemical data for compounds **1**–**4**[a]

	$E_{1/2}(Co^{1+/0})$ (V)	$E_{1/2}(Phen^{1-/0})$ (V)	$E_{1/2}(bpy^{1-/0})$ (V)
1	0.70	−1.32	−1.49
2	0.71	−1.27	−1.52
3		−1.19	−1.54
4		−1.07	−1.51
Ru(bpy)$_3$(PF$_6$)$_2$		−1.36	−1.55

[a] Cyclic voltammograms (CV) and Osteryoung square wave voltammetry (OSWV) were measured in 1 mM acetonitrile solutions containing 0.1 M Bu$_4$NPF$_6$, using a Ag/AgNO$_3$/CH$_3$CN reference electrode (+0.37 V vs. SCE; calibrated with Fc$^{0/+}$) and Pt working. Data were taken from CV at 4.9 V s^{-1} scan rate and OSWV at 298 K.

SCE) described in detail in Section 4. A luminescence emerged as the electrolysis proceeded, and its emission intensity gradually increased as shown in Fig. 3. Under this electrolysis condition, only the dicobalt unit in **1** was oxidized as described in Section 2.3, because the oxidation of the ruthenium center requires a potential higher than 1.0 V vs. SCE. The resultant emission spectra were almost the same as that of precursor complex **3**.

On the other hand, UV–Vis spectral change was more complicated because of the two-step reactions under the electrolysis, followed by a dark reaction after the termination of electrolysis. The observed changes under electrolysis are the increase of the absorption intensity at around 340 nm and the decrease in the wavelength area longer than 370 nm for **1** (Fig. 4). The former area corresponds to the band assignable to the π–$\pi*$(C$\equiv$C) absorption of **3**, and the latter to the broad absorption bands originated from the MMCT and d–d transition on dicobalt unit in **1**, as explained in Fig. 1. However, no further spectral change was observed after 18 h of electrolysis. The final spectrum does not exhibit the gullet around 325 nm that is observed for **3**, as shown in Fig. 1. When solution subjected to 18 h of electric oxidation was left standing at room temperature for 24 h, a spectrum similar to that of **3** was obtained from this dark reaction, as shown in Fig. 4.

These results on emission and absorption spectral changes suggest that the electrolysis of **1** produces a kind of deviant species derived from an EC reaction after the oxidation of the dicobalt unit at first, and the precursor complex **3** is reconstructed. It is surmised that the deviant
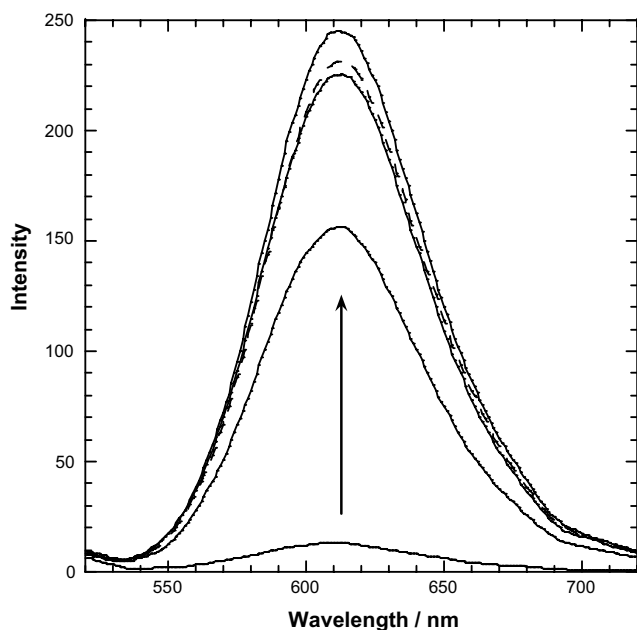

Fig. 4. UV–Vis absorption spectral change of **1** under constant potential electrolysis in CH$_3$CN solution at room temperature. Solid lines (—) show the spectra measured after 5 min, 6 h, 12 h, and 18 h of electrolysis. Arrows show changes in the spectrum step by step, and the dotted line (- - -) is the spectrum of solution left standing for 24 h after electrolysis.
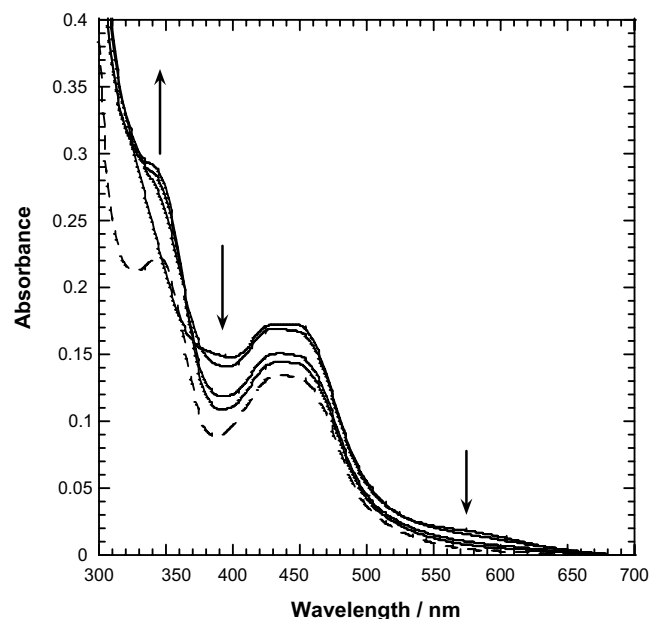
species gradually decomposes to cobalt and dppm under air.

Compound **2** showed a similar luminescence growing under the same electrolysis condition as that of **1**, and the emission spectrum was consistent with that of precursor complex **4**. However, the absorption spectrum close to that of **4** was not detected even in the solution left standing at room temperature for 24 h under air, as in the case of **1** mentioned above. It is quite interesting to point out that the increase in the absorption intensity in the 370 nm region and the decrease in the wavelength area longer than 400 nm were observed in a fashion similar to that of **1** under electrolysis. This difference between **1** and **2** is attributed to their different reaction mechanisms for dark reactions.

3. Conclusion

A novel hybrid system of ruthenium polypyridyl complexes anchored by dicobalt carbonyl units, Ru–Co$_2$ hybrid complexes **1** and **2**, has been successfully prepared from the dicobalt carbonyl complex Co$_2$(CO)$_6$(dppm) and ruthenium complex **3** or **4**, either of which contains phenanthroline with tolylethynyl substituent(s) as a diimine ligand. The spectroscopic data indicate that these Ru–Co$_2$ hybrid complexes have a familiar structure of the type [Co$_2$(alkyne)(CO)$_4$(dppm)]. Precursor complexes **3** and **4** have shown obvious phosphorescence from the ^{3}MLCT excited state. However, the present Ru–Co$_2$ hybrid complexes **1** and **2** are nonluminescent. This spectral characteristic is interpreted in terms of the

Fig. 3. Emission spectral changes of **1** under constant potential electrolysis in CH$_3$CN solution at room temperature. Solid lines (—) show the spectra measured after 5 min, 6 h, 12 h, and 18 h of electrolysis. Arrows show changes in the spectrum step by step, and the dotted line (- - -) is the spectrum of solution left standing for 24 h after electrolysis.

intramolecular energy transfer from the ruthenium polypyridyl unit to the dicobalt carbonyl unit and the subsequent quenching to the ground state by a radiationless deactivation accompanied by a vibrational relaxation on the dicobalt carbonyl unit. The electrochemical data and the spectral changes by the constant potential electrolysis support the intramolecular emission quenching described above and showed the recovery of an emission spectrum similar to that of the precursor complex. It is notable that obvious emission quenching for Ru–Co$_2$ hybrids is revealed here for the first time, although to our knowledge one example of the preparation of ruthenium(II) terpyridyl complexes linked with the Co$_2$(alkyne)(CO)$_6$ unit was reported, but with no photophysical data [27]. This hybrid system of ruthenium polypyridyl complexes anchored by the dicobalt organometallics is quite promising for the photochemical development of intramolecular energy transfer that differs from that of many previously reported bridging systems having Werner-type heteronuclear metal complexes. This system should provide quite a lot of useful insight into a new type of photoenergy conversion system.

4. Experimental

4.1. Materials and general measurements

All reactions were carried out under an argon atmosphere. Solvents were freshly distilled according to standard procedures. The starting materials were purchased from Aldrich or Wako and used without further purification. The Co$_2$(CO)$_6$(dppm) was synthesized by the method of Fukumoto et al. [28]. The precursor ruthenium complexes [Ru(bpy)$_2$(phen–≡–tolyl)](PF$_6$)$_2$ (**3**) and [Ru(bpy)$_2$-(tolyl–≡–phen–≡–tolyl)](PF$_6$)$_2$ (**4**) were prepared by the similar method to our recent report [19]. The characterization of the novel complexes has been done by IR, ESI-MS, UV–Vis, emission spectroscopy, and elemental analyses. IR spectra were obtained on a JASCO FT/IR 460 spectrometer using the KBr-pellet method.

Elemental analyses were carried out at the center for organic elemental microanalysis, graduate school of pharmaceutical sciences, Kyoto University. UV–Vis spectra were recorded on a JASCO V-750 UV/VIS/NIR spectrophotometer and emission spectra were recorded on a JASCO FP-750 in an acetonitrile (spectroscopic grade) at room temperature.

Electrochemical measurements were performed by using a BAS CV-50W Voltammetric Analyzer. Measurements were made in argon-purged acetonitrile containing 0.1 M [N(n–C$_4$H$_9$)$_4$](PF$_6$) in a three-compartment cell. A platinum coil counter, a platinum wire working, and Ag/AgNO$_3$ reference electrode (+0.37 V vs. SCE; calibrated with Fc$^{+/0}$) were used. The $E_{1/2}$ values were obtained by osteryoung square wave voltammetry (OSWV) and calculated as the average of the anodic and cathodic peak potentials, $(E_{pa} + E_{pc})/2$ from cyclic voltammograms (CV) data.

The constant potential electrolysis on **1** or **2** was performed by using a HOKUTO POTENTIOSTAT/GALVANOSTAT HA-151. The electrolysis was done with potential value at 0.98 V vs. SCE and the current at 100 mA by using the acetonitrile solution (40 ml) containing 0.15 mM compound **1** or **2** and 0.1 M [N(n–C$_4$H$_9$)$_4$](PF$_6$) in a three-compartment cell. A platinum wire counter and a platinum sheet working were adapted with a sample folder, and Ag/AgNO$_3$ reference electrodes were used. The solutions (10 μM with respect to the concentration of ruthenium ion) for spectral change measurements of UV–Vis and emission spectra were diluted with the acetonitrile solution at 3 h intervals during 18 h run. The spectral change was no longer detectable after 18 h electrolysis. The solution was left standing for 24 h after the electrolysis was turned off.

4.2. Preparation of [Ru(bpy)$_2${phen–C{Co$_2$(CO)$_4$(dppm)}-C–tolyl}](PF$_6$)$_2$ (**1**)

The Co$_2$(CO)$_6$(dppm) (65 mg, 0.09 mmol) was added to the anhydrous acetonitrile solution (30 ml) of **3** (70 mg, 0.07 mmol) under Ar. After the mixture was heated at 60 °C with stirring for 3 h, the red solution turned to brown. The acetonitrile was distilled off under reduced pressure and the dark brown adduct was precipitated. The precipitate was redissolved in anhydrous THF (50 ml) and the solution was filtered to remove insoluble residues. After removing THF under reduced pressure, the compound was washed with ether (30 ml) several times. The dark brawn powder was dried at 30 °C under vacuum for 12 h. Yield: 94% (106 mg). Anal. Calc. for C$_{70}$H$_{52}$F$_{12}$N$_6$O$_4$P$_4$Co$_2$Ru · 1H$_2$O: C, 51.58; H, 3.34; N, 5.16. Found C, 51.68; H, 3.38; N, 4.88%. IR (cm^{-1})v(CO): 2025 (s), 1996 (vs), 1970 (vs). ^{1}H NMR (300 MHz, CD$_3$CN, ppm): δ 8.59–8.37 (m, 6H, Phen-H2, H9 and bpy-H6, H6′), 8.24–8.17 (m, 3H, Phen-H5, H6, H7), 8.08–7.94 (m, 5H, Phen-H4 and bpy-H5, H5′), 7.80–7.56 (m, 5H, Phen-H8 and bpy-H3, H3′), 7.50–6.90 (m, 28H, bpy-H4, H4′, phenyl-H, and tolyl-H), 3.71–3.49 (m, 1H, P–CH$_2$–P), 3.45–3.33 (m, 1H, P–CH$_2$–P), 2.410 (s, 3H, methyl–H).

4.3. Preparation of [Ru(bpy)$_2${tolyl–C{Co$_2$(CO)$_4$(dppm)}-C–phen–C{Co$_2$(CO)$_4$(dppm)}C–tolyl}](PF$_6$)$_2$ (**2**)

Seventy-three milligrams (0.11 mmol) of Co$_2$(CO)$_6$-(dppm) was added to an anhydrous acetonitrile (10 ml) of **4** (40 mg, 0.036 mmol) under argon. The mixture solution was heated at 60 °C with stirring for 5.5 h. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was collected by filtration with a suction filter, washed with ether (30 ml) several times to remove unreacted Co$_2$(CO)$_6$(dppm), and redissolved in anhydrous THF (30 ml). The insoluble residue was filtered off under argon. The solvent was distilled off from the filtrate under reduced pressure and the dark brawn powder was dried at 30 °C

under vacuum for 5 h. Yield: 76% (64 mg). Anal. Calc. for $C_{108}H_{79}F_{12}N_6O_8P_6Co_2Ru_1H_2O$: C, 55.02; H, 3.46; N, 3.56. Found C, 54.88; H, 3.59; N, 3.47%. IR $(cm^{-1})\nu(CO)$: 2025 (s), 1996 (vs), 1970 (vs). ^1H NMR (300 MHz, CD_3CN, ppm): δ 8.52–8.20 (m, 6H, Phen-H2, H9 and bpy-H6, H6′), 8.08–7.94 (m, 8H, Phen-H4, H5, H6, H7 and bpy-H5, -H5′), 7.80–6.90 (m, 56H, bpy-H3, H3′, H4, H4′, phenyl-H, and tolyl-H), 3.74-3.61 (m, 1H, P–CH₂–P), 3.45–3.32 (m, 1H, P–CH₂–P), 2.412 (s, 3H, methyl–H).

Acknowledgements

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