A Novel Dinuclear Ru(II) Complex Having a Bridging Ligand of a Rigid and Extended Structure: Incorporation of an Anthraquinone Unit and Efficient Emission Quenching

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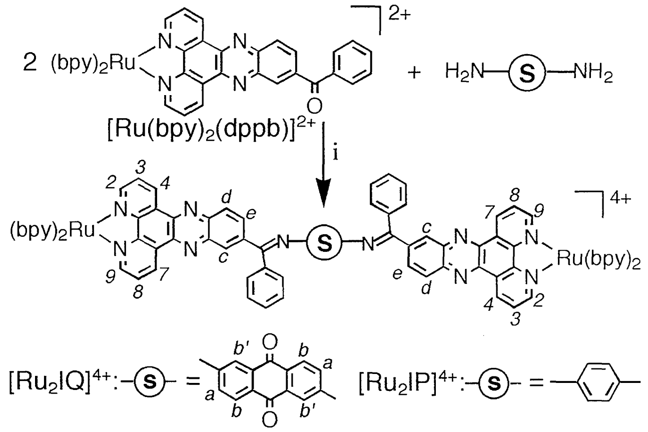
Dinuclear Ru(II) complex having extended conjugation within the bridging ligand was prepared by coupling of the Ru(II) polypyridyl complex having a benzoyl-substituted phenazine unit with diaminoanthraquinone in one step, in which emission from the excited Ru(II) center was efficiently quenched through the anthraquinone unit.

Photo-induced energy or electron transfer processes in supramolecular species[1] are currently the object of much interest in view of the design of photochemical molecular devices.[2] In particular, Ru(II) polypyridyl complexes have been frequently used as building blocks of polynuclear complexes that behave as supramolecular species.[1] However, synthetically, it was found very difficult to assemble these metal complexes in a rigid and extended structure that could facilitate the migration of energy or electron over a long distance. Thus, to achieve this goal in more efficient and predictable way, we developed a novel design of dinuclear Ru(II) complexes having phenazine and anthraquinone units in the bridging ligand.



Scheme 1. Syntheses of dinuclear Ru(II) complexes: i) DMF, AcOH, reflux(3 days).

Synthetic strategy is illustrated in Scheme 1. Various Ru(II) complexes of dipyrido[3,2-a:2′,3′-c]phenazine (dppz) have currently been studied because of their unique luminescent and redox properties.[3] By introducing PhCO- group to the dppz unit (dppb), variety of dinuclear Ru(II) complexes can be prepared in one-step by condensation with various diamino-functionalized connecting units, for which 2,6-diamino-anthraquinone was used as an electron/energy trap in this study. The bridging ligand thus prepared has the extended conjugation through two imine bonds, and the distance from one end to the other (pyrido-nitrogens) is estimated to be 2.3 nm by the MM2 calculation. Moreover, introduction of various functional groups as the connecting unit to the bridging ligand is expected to give unique photochemical properties to the complex. Acid-catalyzed condensation of $[Ru(bpy)_2(dppb)]^{2+}$ with 2,6-diamino-anthraquinone successfully gave the dinuclear complex $[Ru_2IQ]^{4+}$ in moderate yield (51%) after column chromatography (Sephadex LH-20/acetonitrile containing 4 mg/ml NH_4PF_6). The complex obtained as a PF_6 salt was a dark orange powder, and the structure was confirmed by IR and ^{1}H-NMR (^{1}H-^{1}H COSY) spectra, molar conductivity, and elemental analysis.[4] The dinuclear complex $[Ru_2IP]^{4+}$ having a phenyl unit instead of the anthraquinone unit was also prepared as a reference.[4]

Absorption spectra of $[Ru_2IQ]^{4+}$ and $[Ru_2IP]^{4+}$ in acetonitrile at 25 °C showed broad MLCT (metal-to-ligand charge transfer) bands at about 450 nm along with the ligand-centered π-π^* transition at 245-287 nm. However, absorption tail of these complexes extended further to the longer wavelength side compared with their parent complexes,[5] $[Ru(bpy)_2(dppb)]^{2+}$, $[Ru(bpy)_2(dppz)]^{2+}$ and $[Ru(bpy)_3]^{2+}$, indicating presence of the lower-lying π^* orbital due to extension of the π-conjugation from the dppz to the anthraquinone or phenylene unit through the imine bonds.

Emission around 600 nm was observed by excitation of the MLCT band of $[Ru_2IP]^{4+}$ (λ_{ex} = 440 nm) in acetonitrile at 25 °C (Figure 1), which was similar to those of their parent complexes showing that the emission was from the excited Ru(II)-polypyridyl center.[6] Though emission of $[Ru_2IQ]^{4+}$ appeared at the same region, the intensity was very weak. Relative intensity[7] of the emission was only 0.03 of that of $[Ru(bpy)_3]^{2+}$, which was an order of magnitude weaker than that of $[Ru_2IP]^{4+}$. To clarify the role of the anthraquinone unit on the weak emission of $[Ru_2IQ]^{4+}$, solvent effect on the spectra was studied (Table 1). It is well documented that presence of protic solvents induces

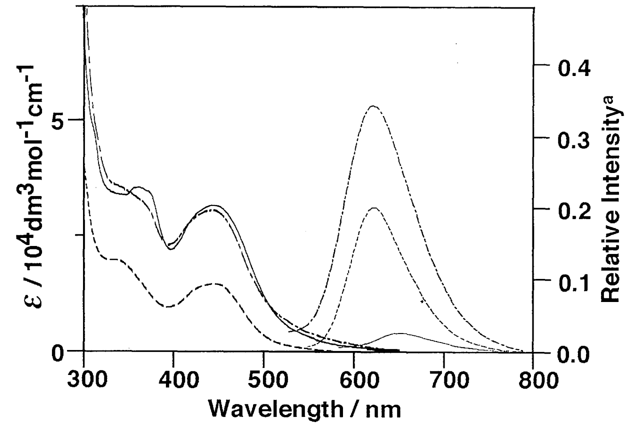


Figure 1. Absorption (1.0×10^{-5} mol dm^{-3}) and emission (1.0×10^{-6} mol dm^{-3}, λ_{ex} = 440 nm) spectra of Ru(II) complexes in acetonitrile at 25 °C: (——)$[Ru_2IQ]^{4+}$, (— — —)$[Ru_2IP]^{4+}$, and (------)$[Ru(bpy)_2(dppb)]^{2+}$, a) see references and notes 7.

Table 1. Solvent effect on the emission intensities of the complexes at 25 °C

complex	relative emission intensity[a]		
	CH_3CN	$CH_3CN:CH_3OH$ =1 : 9 (v/v)	$CH_3CN:H_2O$ =1 : 9 (v/v)
$[Ru(bpy)_2(dppb)]^{2+}$	1(0.20)[b]	0.81	0.69
$[Ru_2IP]^{4+}$	1(0.34)[b]	0.94	0.67
$[Ru_2IQ]^{4+}$	1(0.03)[b]	0.10	no emission 0.56[c]

[a]Relative to those in CH_3CN (λ_{ex} = 440 nm). [b]Values in parentheses represent the intensities relative to that of $[Ru(bpy)_3]^{2+}$ (see references and notes 7). [c]In the presence of 0.05 mol dm^{-3} sodium dodecylsulfate, $CH_3CN : H_2O = 0.1 : 9.9$, v/v.

quenching of the emission of $[Ru(bpy)_2(dppz)]^{2+}$ and anthraquinone derivatives through hydrogen bonding to the phenazine ring nitrogens[3b] and quinone oxygens,[8] respectively. The emission of $[Ru_2IQ]^{4+}$ was further quenched in methanolic solvent and no emission was observed in an acetonitrile (10%)-containing aqueous solution. However, presence of anionic micelles of sodium dodecylsulfate (average diameter 2-3 nm) in the aqueous solution restored roughly half of the emission in acetonitrile. Therefore, hydrogen bonding to the bridging ligand is responsible for the emission quenching of $[Ru_2IQ]^{4+}$ in the protic solvents. Table 1 shows extent of the quenching effect on the related complexes. Intensities in protic solvents are given as relative to those in acetonitrile. The parent complex, $[Ru(bpy)_2(dppb)]^{2+}$, suffered small quenching in methanolic and moderate quenching in aqueous solutions, and $[Ru_2IP]^{4+}$ having no anthraquinone unit suffered similar solvent-induced quenching. However, $[Ru_2IQ]^{4+}$ showed drastic solvent-induced quenching. Hydrogen bonding to the phenazine ring nitrogens alone can not explain this large quenching effect. Since structural difference between $[Ru_2IQ]^{4+}$ and $[Ru_2IP]^{4+}$ is only the connecting unit, the hydrogen bonding to the quinone oxygens rather than to the phenazine ring nitrogens is responsible to the observed solvent-induced quenching effect of $[Ru_2IQ]^{4+}$. These results suggest that the emission from the excited Ru(II)-polypyridyl center was efficiently quenched through the anthraquinone unit.

In this study, we presented the novel design of the dinuclear Ru(II) complexes having the extended conjugation within the bridging ligand in order to facilitate energy and/or electron migration, and the method offers the way to incorporate variety of functional units within the bridging ligand by selection of diamino-functionalized compounds (Scheme 1). In the case of the anthraquinone-incorporated complex, $[Ru_2IQ]^{4+}$, energy or electron migration within the bridging ligand induced efficient quenching of the excited Ru(II) center through the anthraquinone unit.[9,10] Detailed mechanism of the emission quenching and preparation of variety of homo- and hetero-dinuclear Ru(II) and Os(II) complexes having different connecting units are now underway in our laboratory.

References and Notes

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4 **$[Ru_2IQ](PF_6)_4 \cdot 4H_2O$:** dark orange powder; IR (KBr, cm^{-1}) $\upsilon_{C=N}$ 1630; ^{1}H-NMR (acetone-d_6, 270 MHz, see Scheme 1) δ, ppm: 7.43 (t; 4H, 6,6'- bipyridine, J = 6.0 Hz), 7.63-7.69 (m; 4H, m-phenyl; 4H, 6,6'- bipyridine), 7.76-7.82 (m; 2H, p-phenyl), 7.96 (d; 4H, o-phenyl, J = 7.4 Hz), 8.06-8.20 (m; 8H, 5,5'-bipyridine; 8H, 4,4'-bipyridine; 4H, 3,8-phenazine), 8.28 (t; 4H, d,e; 1H, c, J = 7.8 Hz), 8.43-8.62 (m; 4H, 2,9-phenazine; 4H, a,b; 1H, c), 8.70 (d; 2H, b', J = 2.2 Hz), 8.86 (t; 8H, 3,3'-bipyridine, J = 8.5 Hz), 9.70-9.77 (m; 4H, 4,7-phenazine); Anal. Found: C, 51.02; H, 3.28; N, 9.70%; Calcd. for $C_{104}H_{74}N_{18}F_{24}O_6P_4Ru_2$ including 4 mol water: C, 50.91; H, 3.04; N, 10.27%; Conductivity Λ_M = 625 Ω^{-1} cm^2 mol^{-1} dm^3 (at 25 °C). **$[Ru_2IP](PF_6)_4 \cdot 6H_2O$:** dark orange powder; IR (KBr, cm^{-1}) $\upsilon_{C=N}$ 1636; ^{1}H-NMR (acetone-d_6, 400 MHz) δ, ppm: 7.42-7.45 (m, 5H), 7.65-7.81 (m, 13H), 7.98-8.31 (m, 25H), 8.51-8.68 (m, 6H), 8.77-8.91 (m, 11H), 9.76-9.83 (m, 4H); Anal. Found: C, 48.91; H, 3.49; N, 10.03%; Calcd. for $C_{96}H_{76}N_{18}F_{24}O_6P_4Ru_2$ including 6 mol water: C, 48.86; H, 3.25; N, 10.68%; Conductivity Λ_M = 537 Ω^{-1} cm^2 mol^{-1} dm^3 (at 25 °C).

5 Though data is not included in this letter, we prepared a dinuclear Ru(II) complex in which the anthraquinone unit was connected to the dppz units through amide bonds instead of imine bonds. Absorption tail of this complex was extended only up to 570 nm.

6 Excitation spectra monitored at 650 nm was similar to the absorption spectra.

7 Emission intensities of the sample solutions (1.0 x 10^{-6} mol dm^{-3}, λ_{ex} = 440 nm) were normalized by their absorbance at 440 nm, and were reported relative to that of $[Ru(bpy)_3]^{2+}$ in aqueous solution.

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10 $E_{1/2}$ of $[Ru_2IQ]^{4+}$ (0.1 mol dm^{-3} $(C_4H_9)_4NClO_4$ in CH_3CN, V vs SCE): 1.32(Ru(III)/Ru(II)), -0.76(dppz), -1.03 (anthraquinone), -1.29(bpy), -1.42(bpy). Emission quenching by electron transfer from the excited Ru(II) center to the anthraquinone has well established.[9] Though $E_{1/2}$ of the dppz was higher than that of the anthraquinone unit in our complex, emission quenching by electron transfer to the anthraquinone unit can not be excluded because the redox orbital of the dppz was indicated to be separated from the optical orbital.[3c]