Novel Intramolecular Electron-transfer Equilibrium in a Spatially Interaction Binary System of a Metal-free Porphyrin and a Ruthenium Trichloro Terpyridyl Complex

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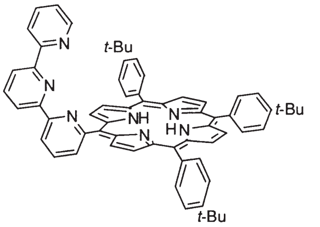
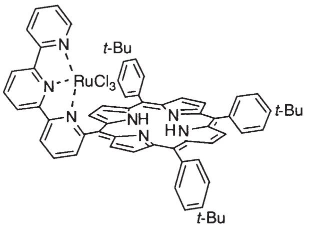
Temperature-dependent reversible intramolecular electron transfer between a Ru(III)–porphyrin and a Ru(II)–porphyrin π-cation radical was observed in a novel binary π-system of a porphyrin and a ruthenium trichloro terpyridyl complex.

Long-established studies on π-cation radicals of metalloporphyrins have contributed to the understanding of biological redox systems.[1] In contrast, π-cation radicals of metal-free porphyrins have never been isolated because of their much shorter life times compared to that of the metalloporphyrins.[2,3] Here we report a novel reversible intramolecular electron transfer in a trichlororuthenium complex of 5-(2-terpyridyl)-10,15,20-tri(4-*tert*-butylphenyl)porphyrin, $RuCl_3(terpyPH_2)$ in solution, causing an equilibrium between two paramagnetic species, a Ru(III)–neutral porphyrin and a Ru(II)–porphyrin π-cation radical. This novel electron-transfer equilibrium between the two paramagnetic species was realized by use of the new ligand, $terpyPH_2$ with a binary system of a porphyrin and a terpyridine, and by insertion of $RuCl_3$ to the terpyridyl moiety leading a Cl ligand into locating close to both the ruthenium ion and the porphyrin ring.



$terpyPH_2$



$RuCl_3(terpyPH_2)$

The new porphyrin, $terpyPH_2$,[4] was synthesized by refluxing pyrrole (6.0 equiv.), 4-*tert*-butylbenzaldehyde (5.0 equiv.), and 2-formylterpyridine (1.0 equiv.) in propionic acid in 21% yield based on 2-formylterpyridine.[5] A metallation of the terpyridyl moiety was carried out under refluxing $terpyPH_2$ (769 mg, 0.819 mmol) and $RuCl_3{\cdot}3H_2O$ (265 mg, 1.23 mmol) in ethanol/chloroform (4:1 v/v) for 1 day. The product, $RuCl_3(terpyPH_2)$,[4] was eluted from a silica gel column (activity III–IV) with dichloromethane/methanol (10:1 v/v) as a dark red second band in 85% yield. IR and UV-vis spectral data for $RuCl_3(terpyPH_2)$ are consistent with the selective insertion of a ruthenium ion to the terpyridyl moiety as follows: (1) the feature of the C–C stretching IR bands of the terpyridyl aromatic ring around $1600\,cm^{-1}$ was changed; (2) the N–H stretching IR band of the porphyrin moiety at $3315\,cm^{-1}$ did not disappear; (3) four Q-bands characteristic of metal-free porphyrins existed at 521, 555, 595, and 652 nm in the visible spectrum of $RuCl_3(terpyPH_2)$ (Figure 1). The Soret band of the ruthenium complex at $\lambda_{max} = 423\,nm$ ($\varepsilon = 2.0 \times 10^5\,mol^{-1}dm^3\,cm^{-1}$) was much weaker in intensity than that of $terpyPH_2$ at 422 nm ($4.2 \times 10^5\,mol^{-1}dm^3\,cm^{-1}$) in benzene, indicating the effects of the metallation of the terpyridyl moiety on the electronic states of the porphyrin moiety.

A curious phenomenon observed in the UV-vis spectrum of $RuCl_3(terpyPH_2)$ in benzonitrile is the appearance of a weak shoulder band beside the Soret band in the longer wavelength region and broad absorption over 600–700 nm. The absorption bands decrease in intensity when the temperature is raised. This temperature-dependent spectral change is reversible between 20 and 70 °C (Figure 1). The difference in the spectrum at 20 and at 70 °C (Figure 1, inset) shows absorption peaks at 455, 624, and 679 nm, which are nearly consistent with those of a π-cation radical of a metal-free 5,10,15,20-tetraphenylporphyrin, $H_2TPP^{+\bullet}$, prepared by photochemical oxidation in a glassy solution at 79 K.[2] Intriguingly, a weak broad absorption band ($\varepsilon = 560\,mol^{-1}dm^3\,cm^{-1}$ at 900 nm) was observed over 800–1500 nm in the near-IR region in benzonitrile. This low-energy band is probably due to valence tautomerization;[6] that is photo-induced intramolecular electron exchange between the Ru(III)–neutral porphyrin and the Ru(II)–porphyrin π-cation radical.

The ESR spectrum of the isolated solid of $RuCl_3(terpyPH_2)$ at 7.0 K is characterized by the superposition of a sharp signal

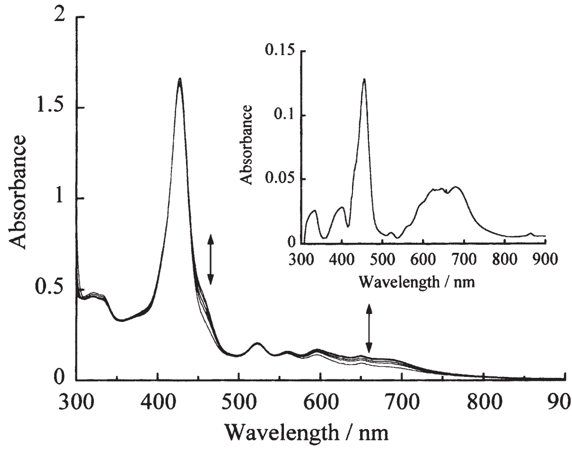
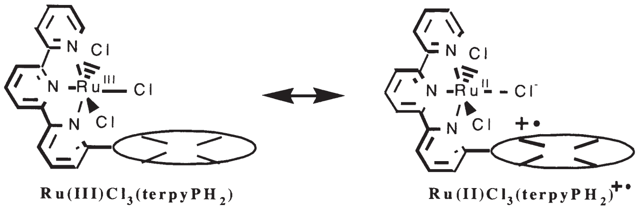


Figure 1. (a) Temperature-dependent UV-vis absorption spectal change of $RuCl_3(terpyPH_2)$ ($1.50 \times 10^{-4}\,mol\,dm^{-3}$) in benzonitrile within the range of 20 and 70 °C. Inset: the difference in the spectra between 20 and 70 °C.



Scheme 1. Electron transfer equilibrium in $RuCl_3(terpyPH_2)$.

($g = 2.001$) and broad signals ($g_1 = 2.36$, $g_2 = 2.21$, and $g_3 = 1.85$). The ESR signals of a frozen benzonitrile solution of $RuCl_3(terpyPH_2)$ near liquid helium temperature are similar to those of the solid sample. The former signal is ascribable to a porphyrin π-cation radical,[1,2,7] and the latter signals are an axial pattern of Ru(III) species.[8] A similar sharp signal of $H_2TPP^{+\bullet}$ ($g = 2.0024$) was observed only in rigid glass at low temperature around 90 K.[2] The UV-vis and ESR spectroscopic results noted above indicate a novel temperature-dependent intramolecular electron transfer between two paramagnetic species, Ru(III)–neutral porphyrin and Ru(II)–porphyrin π-cation radical, as given in Scheme 1.

The left species, $Ru(III)Cl_3(terpyPH_2)$, is more dominant at higher temperature in the thermal equilibrium. It should be noted that the intensities of the ESR signals of two paramagnetic components, the Ru(III) nucleus and the porphyrin π-cation radical, gradually decreased when the temperature was raised. This is probably caused by decrease in the porphyrin π-cation radical through the thermal equilibrium, and increase in the Ru(III) component having a large spin-orbit interaction, which leads to the fast spin relaxation.

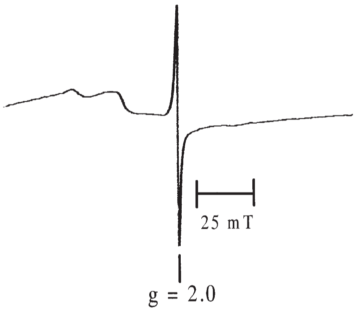


Figure 2. An ESR spectrum of the solid state of $RuCl_3(terpyPH_2)$ at 7.0 K.

A cyclic voltammogram of $terpyPH_2$ in dichloromethane shows two reversible reduction waves at $E^{0'} = -1.65$ and -1.98 V vs ferrocenium/ferrocene (Fc^+/Fc), and one irreversible reduction wave at $E_{pc} = -2.31$ V, which are assigned to two successive one-electron reductions of the porphyrin moiety and a one-electron reduction of the terpyridyl moiety, respectively (Figure 3a).[9] The two irreversible oxidation waves at $E_{pa} = 0.52$ and 0.72 V are due to two successive one-electron oxidations of the porphyrin moiety, similar to that occurs in other *meso*-tetraphenylporphyrins.[2,3] In a cyclic voltammogram of $RuCl_3(terpyPH_2)$ in dichloromethane, four reversible waves are observed within −1.0 and 0.3 V, where the quasi-reversible wave appears at $E^{0'} = -0.04$ V (Figure 3, inset). Controlled-potential oxidation of $RuCl_3(terpyPH_2)$ in dichloromethane at 0.3 V resulted in an increase of the UV-vis absorption bands at 450 and 676 nm characteristic of the metal-free porphyrin π-cation radical, indicating a formation of $Ru(III)Cl_3(terpyPH_2^{+\bullet})$. The oxidation at 0.8 V led to a drastic absorption spectral change showing the formation of a two-electron oxidized form of the porphyrin moiety, indicating a formation of $Ru(III)Cl_3(terpyPH_2^{2+})$, at $E_{pa} = 0.64$ V. It should be noted that a similar spectral change was observed by two-electron oxidation of $terpyPH_2$ at 1.0 V to form the dication, $terpyPH_2^{2+}$.[3]

One of three Cl ligands in $RuCl_3(terpyPH_2)$ locates closely above the porphyrin plane, according to the molecular calculation using MM+. The distance between the Cl ligand and the nearest carbon atom of the porphyrin moiety is estimated to be 2.9 Å. The one-electron oxidation of the porphyrin moiety of $RuCl_3(terpyPH_2)$ occurs at −0.04 V, which is 0.60 V more negative potential than that of $terpyPH_2$ to generate $terpyPH_2^{+\bullet}$. The interaction between the Cl ligand and π-orbitals of the porphyrin moiety is probably responsible for the facile oxidation of the porphyrin moiety. If the Cl ion acts as either the ligand for the ruthenium ion or as the counter ion for the porphyrin π-cation radical, a slight atomic motion of the Cl ligand should, in the most plausible mechanism, mediate reversible electron-transfer equilibrium between Ru(III) center and the porphyrin π-cation radical to generate the stable metal-free porphyrin π-cation radical in solution under ambient conditions (Scheme 1).

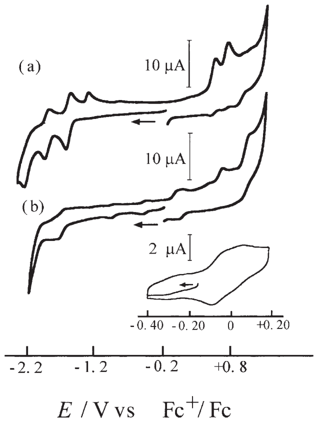


Figure 3. Cyclic voltammograms of $terpyPH_2$ (a) and $RuCl_3(terpyPH_2)$ (b) in 0.1 M Bu_4NClO_4–dichloromethane at $0.1\,V\,s^{-1}$. Inset: a voltammogram of $RuCl_3(terpyPH_2)$ between −0.2 and +0.4 V.

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4 *Characterisation data*: $terpyPH_2$; Anal. Calcd. for $C_{65}H_{59}N_7$: C, 83.21; H, 6.34; N, 10.45%. Found: C, 82.99; H, 6.54; N, 10.24%. MALDI-TOF MS; *m/z* 939.2 ($[M + H]^+$). ^1H NMR (chloroform-*d*) δ 9.02 (dd ($J = 3.5$, 3.5 Hz), 1H), 8.94 (d (2.6), 4H), 8.88 (s, 4H), 8.81 (d (7.9), 1H), 8.75 (d (4.0), 1H), 8.67 (dd (7.6, 1.0), 1H), 8.49 (dd (7.6, 1.0), 1H), 8.25–8.27 (m, 2H), 8.15 (d (8.3), 6H), 7.96 (td (7.6, 2.0), 1H), 7.88 (t (7.6), 1H), 7.76 (d (8.3), 6H), 7.38 (td (4.6, 1.0), 1H), 1.61 (s, 9H), 1.60 (s, 18H), −2.68 (s, 2H). $RuCl_3(terpyPH_2)$; Anal. Calcd. for $C_{65}H_{59}N_7RuCl_3$: C, 68.15; H, 5.19; N, 8.56%. Found: C, 67.94; H, 5.46; N, 8.30%. MALDI-TOF MS; *m/z* 1038.0 ($[M - 3Cl - H]^-$).

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