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Tetrahedron Letters
Tetrahedron Letters 48 (2007) 5970–5972

Redox-switchable conjugated bimetallic ruthenium(II) complexes

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Received 14 May 2007; revised 20 June 2007; accepted 21 June 2007
Available online 29 June 2007

Abstract—The conjugated bimetallic ruthenium(II) complex composed of 1,4-phenylenediamine as a bridging ligand was synthesized by photo-irradiation to show redox-switching of the emission properties of the terminal Ru(II) units depending on the redox state of the π-conjugated bridging spacer.

Considerable attention has been devoted to the development of efficient molecular luminescence switching systems because of high sensitivity and easy detection of luminescence signals.[1] Polynuclear bipyridyl ruthenium(II) complexes connected by a bridging spacer have been investigated electrochemically and photophysically to provide electronic and photo-active devices,[2,3] but redox-active bridging spacers have been focused on only in some cases.[1a,d,4] The redox-active phenylenediamine exists in three redox forms: the neutral phenylenediamine, the partially oxidized phenylenediamine radical cation, and the oxidized quinonediimine, which possesses binding capability to transition metals. Photophysical properties of ruthenium(II) complexes are expected to be controlled by the combination with the redox-active *p*-phenylenediamines. From these points of view, we embarked upon the design of the conjugated bimetallic ruthenium(II) complex composed of 1,4-phenylenediamine as a bridging ligand to provide a novel redox-switching system for the emission properties.

Photo-irradiation of (acetonitrile)(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpy)(CH_3CN)](PF_6)_2$, (**1**) in the presence of 1,4-phenylenediamine (pd) led to the one-pot formation of the conjugated ruthenium(II) complex $\mathbf{2}_{red}$, $[(tpy)(bpy)Ru(pd)Ru(tpy)(bpy)](PF_6)_4$, in 76%.[5] Metal-to-ligand charge transfer (MLCT) transition of $\mathbf{2}_{red}$ shifted to a lower energy relative to **1** as shown in Figure 1, which is considered to be attributed to the electron donating properties of the 1,4-phenylenediamine bridging spacer. The conjugated ruthenium(II) complex $\mathbf{2}_{red}$ was readily oxidized with $Pb(OAc)_4$ to give the quinonediimine (qd) derivative $\mathbf{2}_{ox}$, $[(tpy)(bpy)Ru(qd)Ru(tpy)(bpy)](PF_6)_4$, as an oxidized form (Scheme 1).[6] Furthermore, the oxidized form $\mathbf{2}_{ox}$ could be reduced to the reduced form $\mathbf{2}_{red}$ on treatment with $NH_2NH_2 \cdot H_2O$. The oxidized complex $\mathbf{2}_{ox}$ showed the MLCT band at a higher energy relative to the reduced one $\mathbf{2}_{red}$, probably due to the decrease of the electron donating properties of the bridging spacer (Fig. 1). The strong absorption around 650 nm of $\mathbf{2}_{ox}$ might be assignable to a MLCT band with the quinonediimine moiety.

The single-crystal X-ray structure determination of the conjugated ruthenium(II) complex $\mathbf{2}_{red}$ revealed that

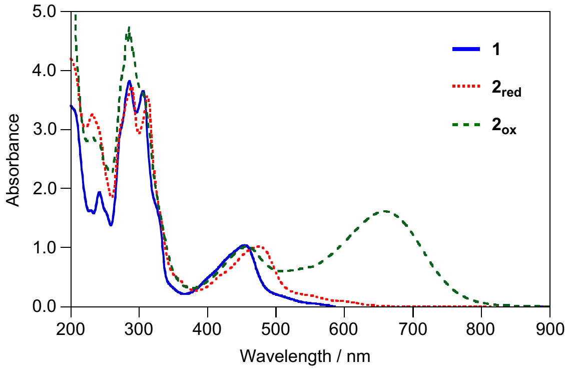

Figure 1. Electronic spectra of **1** (1.0×10^{-4} M), $\mathbf{2}_{red}$ (5.0×10^{-5} M), and $\mathbf{2}_{ox}$ (5.0×10^{-5} M) in MeCN.

Keywords: Conjugated bimetallic ruthenium(II) complex; π-Conjugated bridging spacer; 1,4-Phenylenediamine; Emission properties; Redox-switching.

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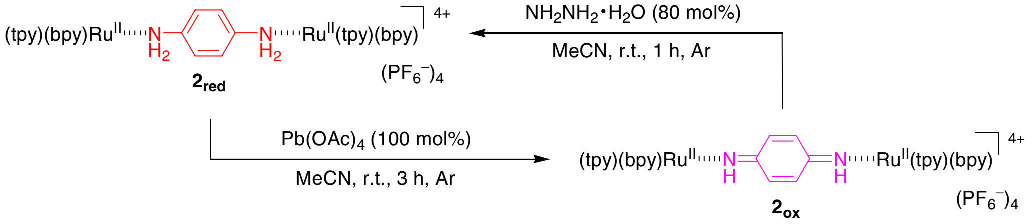
doi:10.1016/j.tetlet.2007.06.133



Scheme 1. Redox interconversion between $\mathbf{2}_{\mathrm{red}}$ and $\mathbf{2}_{\mathrm{ox}}$.

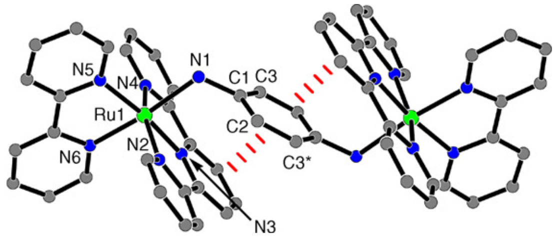


Figure 2. Molecular structure of $\mathbf{2}_{\mathrm{red}}$ (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.192(4), Ru(1)–N(2) 2.076(3), Ru(1)–N(3) 1.965(4), Ru(1)–N(4) 2.077(3), Ru(1)–N(5) 2.087(4), Ru(1)–N(6) 2.037(4), N(1)–C(1) 1.445(7), C(1)–C(2) 1.384(5), C(1)–C(3) 1.378(6), C(2)–C(3*) 1.383(7); N(1)–Ru(1)–N(2) 88.9(1), N(1)–Ru(1)–N(3) 91.5(1), N(1)–Ru(1)–N(5) 94.4(1), N(1)–Ru(1)–N(6) 173.0(1), Ru(1)–N(1)–C(1) 115.8(2), N(1)–C(1)–C(2) 119.4(4).

the two [(tpy)(bpy)Ru] units are bridged by the 1,4-phenylenediamine spacer to form the conjugated complex in an *anti* configuration as depicted in Figure 2.[7] It should be noted that the phenylene plane of the 1,4-phenylenediamine spacer is sandwiched in between the two terpyridyl moieties of each [(tpy)(bpy)Ru] unit through π–π interaction, resulting in the observed torsion angle (Ru(1)–N(1)–C(1)–C(2) = 89.5(3)°).

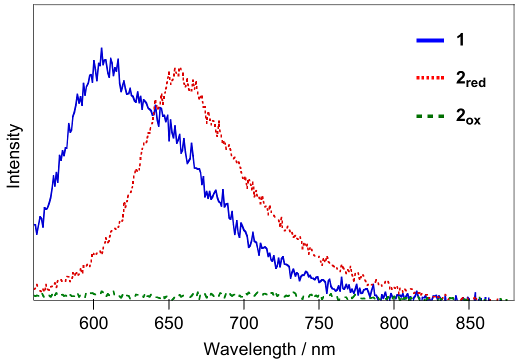
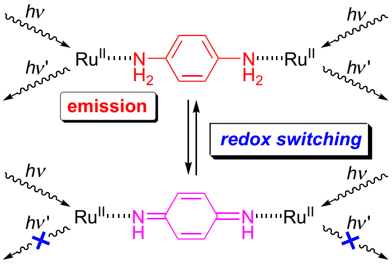


Figure 3. Emission spectra of **1** ($\lambda_{\mathrm{exc}} = 454$ nm, 1.0×10^{-4} M, 298 K), $\mathbf{2}_{\mathrm{red}}$ ($\lambda_{\mathrm{exc}} = 475$ nm, 5.0×10^{-5} M, 298 K), and $\mathbf{2}_{\mathrm{ox}}$ ($\lambda_{\mathrm{exc}} = 457$ nm, 5.0×10^{-5} M, 298 K) in MeCN.



Scheme 2. Schematic representation of the redox-switching of the emission properties of the terminal Ru(II) units.

The emission spectrum of the conjugated ruthenium(II) complex $\mathbf{2}_{\mathrm{red}}$ in acetonitrile showed an emission band at 657 nm (**1**: $\phi = 4.5 \times 10^{-4}$, $\mathbf{2}_{\mathrm{red}}$: $\phi = 4.1 \times 10^{-4}$) as shown in Figure 3. On the contrary to $\mathbf{2}_{\mathrm{red}}$, in the emission spectrum of the quinonediimine derivative $\mathbf{2}_{\mathrm{ox}}$, almost complete quenching was observed. Photo-induced energy transfer is likely to operate in the complex $\mathbf{2}_{\mathrm{ox}}$. These findings indicate that 'on' or 'off' redox switching of the emission properties of the Ru(II) units was achieved by the redox control of the bridging spacer (Scheme 2).

In conclusion, the conjugated bimetallic ruthenium(II) complexes composed of the redox-active π-conjugated bridging ligand was designed. The emission properties of the Ru(II) units were demonstrated to be switched completely 'on' or 'off' by regulating the redox state of the spacer. The present switching system by utilization of coordination and redox properties of π-conjugated bridging ligands is considered to provide a useful approach to the molecular switching materials. Future work will focus on further refinement of redox-active systems and application to efficient molecular devices.

Acknowledgements

This work was financially supported in part by the Shorai Foundation for Science and Technology. Thanks are due to the Analytical Center, Graduate School of Engineering, Osaka University, for the use of the NMR instruments.

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5. Photo-irradiation (Xe lump) of a stirred mixture of **1** (164.3 mg, 0.2 mmol) and 1,4-phenylenediamine (10.8 mg, 0.1 mmol) in dichloromethane (70 mL) under argon at room temperature for 7 h. In the reaction course, a brown solid precipitated. Filtration and washing with dichloromethane afforded the conjugated ruthenium(II) complex $\mathbf{2}_{\mathrm{red}}$ in 76% yield. The conjugated ruthenium(II) complex $\mathbf{2}_{\mathrm{red}}$ was isolated by recrystallization from acetone–diethyl ether. $\mathbf{2}_{\mathrm{red}}$: mp 256–257 °C (decomp.); IR (KBr) 3430, 1603, 1516, 1449, 843, 765, 558 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.52 (d, 2H, $J = 5.4$ Hz), 8.90 (d, 2H, $J = 8.4$ Hz), 8.60 (d, 2H, $J = 8.4$ Hz), 8.43 (dt, 2H, $J = 1.2$, 8.4 Hz), 8.36 (d, 4H, $J = 7.8$ Hz), 8.29 (d, 4H, $J = 8.4$ Hz), 8.19 (ddd, 2H, $J = 0.6$, 5.4, 8.4 Hz), 7.96 (ddd, 4H, $J = 1.2$, 7.8, 8.4 Hz), 7.89 (t, 2H, $J = 7.8$ Hz), 7.77 (ddd, 2H, $J = 1.2$, 7.2, 8.4 Hz), 7.67 (ddd, 4H, $J = 0.6$, 1.2, 5.4 Hz), 7.40 (ddd, 4H, $J = 1.2$, 5.4, 7.8 Hz), 7.05 (ddd, 2H, $J = 1.2$, 6.0, 7.2 Hz), 6.92 (ddd, 2H, $J = 0.6$, 1.2, 6.0 Hz), 6.39 (s, 4H), 5.04 (s, 4H); ^{13}C NMR (150 MHz, DMSO-d_6) 157.7, 157.4, 156.9, 155.7, 153.3, 151.7, 150.8, 137.8, 137.5, 136.9, 136.3, 134.5, 127.5, 126.8, 126.7, 124.1, 123.6, 122.5, 118.7 ppm; FAB-MS *m*/*z* 1524 $(\mathrm{M}\text{-}\mathrm{PF}_6)^+$; Anal. Calcd for $\mathrm{C}_{56}\mathrm{H}_{46}\mathrm{N}_{12}\mathrm{P}_4\mathrm{F}_{24}\mathrm{Ru}_2 2\mathrm{H}_2\mathrm{O}$: C, 39.45; H, 2.96; N, 9.86. Found: C, 39.10; H, 2.80; N, 9.79.
6. A mixture of the conjugated ruthenium(II) complex $\mathbf{2}_{\mathrm{red}}$ (50.1 mg, 0.03 mmol) and $\mathrm{Pb(OAc)}_4$ (13.3 mg, 0.03 mmol) was stirred in acetonitrile (30 mL) under argon at room temperature for 3 h. After evaporation of the solution, the conjugated ruthenium(II) complex $\mathbf{2}_{\mathrm{ox}}$ was isolated quantitatively as a green solid by reprecipitation from acetonitrile and diethyl ether. $\mathbf{2}_{\mathrm{ox}}$: mp 258–259 °C (decomp.); IR (KBr) 3429, 1449, 842, 765, 558 cm^{-1}; ^{1}H NMR (600 MHz, acetone-d_6) δ 11.60 (s, 2H, *syn*), 11.58 (s, 2H, *anti*), 9.21 (ddd, 2H, $J = 0.6$, 1.2, 5.4 Hz, *syn*), 9.15 (ddd, 2H, $J = 0.6$, 1.2, 5.4 Hz, *anti*), 8.93 (ddd, 2H, $J = 0.6$, 1.2, 8.4 Hz, *syn*), 8.88 (ddd, 2H, $J = 0.6$, 1.2, 8.4 Hz, *anti*), 8.75 (d, 4H, $J = 8.4$ Hz, *anti*), 8.74 (d, 4H, $J = 8.4$ Hz, *syn*), 8.72 (ddd, 2H, $J = 0.6$, 1.2, 8.4 Hz, *syn*), 8.68 (ddd, 2H, $J = 0.6$, 1.2, 8.4 Hz, *anti*), 8.62 (ddd, 4H, $J = 0.6$, 1.2, 9.0 Hz, *anti*), 8.60 (ddd, 4H, $J = 0.6$, 1.2, 9.0 Hz, *syn*), 8.45 (ddd, 2H, $J = 1.2$, 7.2, 8.4 Hz, *syn*), 8.39 (t, 2H, $J = 8.4$ Hz, *anti*), 8.38 (t, 2H, $J = 8.4$ Hz, *syn*), 8.37 (ddd, 2H, $J = 1.2$, 7.2, 8.4 Hz, *anti*), 8.15 (ddd, 4H, $J = 1.2$, 7.2, 9.0 Hz, *syn*), 8.08 (ddd, 4H, $J = 1.2$, 7.2, 9.0 Hz, *anti*), 8.06 (ddd, 2H, $J = 1.2$, 5.4, 7.2 Hz, *syn*), 8.02 (ddd, 4H, $J = 0.6$, 1.2, 5.4 Hz, *anti*), 7.99 (ddd, 2H, $J = 1.2$, 7.2, 8.4 Hz, *syn*), 7.98–7.96 (m, 6H, *syn* and *anti*), 7.89 (ddd, 2H, $J = 1.2$, 5.4, 7.2 Hz, *anti*), 7.63 (ddd, 2H, $J = 0.6$, 1.2, 5.4 Hz, *syn*), 7.58 (ddd, 2H, $J = 0.6$, 1.2, 5.4 Hz, *anti*), 7.48 (ddd, 4H, $J = 1.2$, 5.4, 7.2 Hz, *syn*), 7.42 (ddd, 4H, $J = 1.2$, 5.4, 7.2 Hz, *anti*), 7.25 (ddd, 2H, $J = 1.2$, 5.4, 7.2 Hz, *syn*), 7.24 (ddd, 2H, $J = 1.2$, 5.4, 7.2 Hz, *anti*), 6.85 (d, 2H, $J = 1.8$ Hz, *syn*), 6.81 (d, 2H, $J = 10.2$ Hz, *anti*), 6.53 (d, 2H, $J = 10.2$ Hz, *anti*), 6.48 (d, 2H, $J = 1.8$ Hz, *syn*); ^{13}C NMR (150 MHz, acetone-d_6) 175.7, 175.3, 159.4, 158.4, 158.3, 157.4, 157.0, 156.9, 154.7, 154.6, 153.4, 151.5, 151.3, 139.9, 139.3, 139.1, 139.0, 138.9, 138.4, 134.7, 133.5, 129.1, 129.0, 128.8, 128.7, 128.3, 127.9, 127.0, 125.6, 125.5, 125.4, 124.7, 124.6, 124.5 ppm; FAB-MS *m*/*z* 1522 $(\mathrm{M}\text{-}\mathrm{PF}_6)^+$; Anal. Calcd for $\mathrm{C}_{56}\mathrm{H}_{44}\mathrm{N}_{12}\mathrm{P}_4\mathrm{F}_{24}\mathrm{Ru}_2\cdot 4\mathrm{H}_2\mathrm{O}$: C, 38.68; H, 3.01; N, 9.66. Found: C, 38.46; H, 2.69; N, 9.50.
7. *Crystal data for* $\mathbf{2}_{\mathrm{red}}$: $\mathrm{C}_{56}\mathrm{H}_{46}\mathrm{N}_{12}\mathrm{P}_4\mathrm{F}_{24}\mathrm{Ru}_2\cdot 2\mathrm{CH}_3\mathrm{COCH}_3$, $M = 1785.22$, monoclinic, space group $C2/c$ (No. 15), $a = 25.0846(7)$ Å, $b = 16.1689(4)$ Å, $c = 22.3206(7)$ Å, $\beta = 120.2007(6)°$, $V = 7824.2(4)$ Å^3, $Z = 4$, $T = 4.0$ °C, $D_{\mathrm{calc}} = 1.515$ g cm^{-3}, $\mu(\mathrm{Mo\,K}\alpha) = 5.73$ cm^{-1}, Mo Kα radiation ($\lambda = 0.71069$ Å), $R_1 = 0.057$, $wR_2 = 0.178$. CCDC-638146. Crystallographic data (excluding structure factors) for the structures reported in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-638146 for $\mathbf{2}_{\mathrm{red}}$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].