Ruthenium complexes bearing π-conjugated pendant moieties for a redox-switching system

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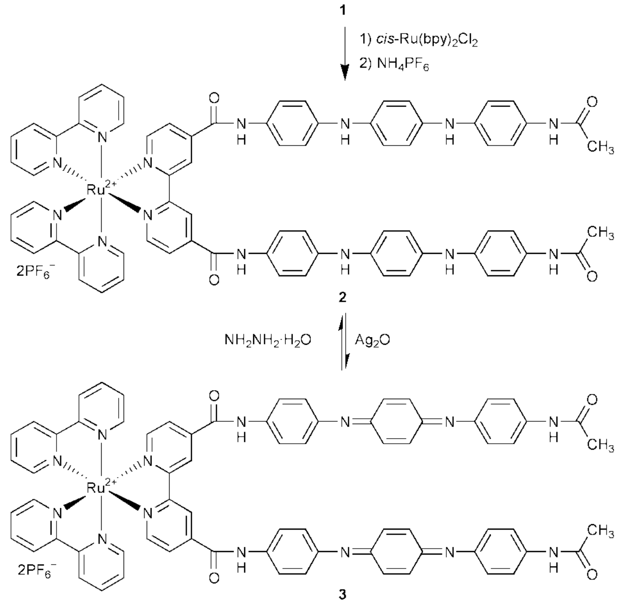
A ruthenium(II) complex bearing *N*,*N*′-bis(4-aminophenyl)-1,4-phenylenediamine moieties, which can be chemically oxidized to the corresponding *N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinonediimine moieties, was synthesized, characterized electrochemically and photochemically, and found to afford a redox-switching system.

The construction of efficient systems for electron transfer is a key factor in the development of versatile catalysts and functionalized materials. Photoinduced electron-transfer systems have been investigated with a variety of ruthenium bipyridyl complexes. A ruthenium complex bearing a redox-active moiety provides an electro-photoswitching device, as exemplified by complexes bearing a benzoquinone[1] or viologen function.[2] Ruthenium(II) complex systems have also been recognized as receptors for anion recognition[3] and photosynthetic models.[4] In a previous paper, quinonediimine derivatives were revealed to afford redox-active catalysts and d,π-conjugated complexes.[5] Furthermore, four π-conjugated pendant groups have been incorporated into a porphyrin scaffold to give atropisomeric three-dimensionally oriented redox-active systems.[6] We herein report redox-switchable ruthenium(II) complexes bearing π-conjugated pendant moieties.

A bipyridyl ligand **1** bearing aniline trimer pendant groups was prepared by amidation of the acid chloride derivative of 2,2′-bipyridine-4,4′-dicarboxylic acid with 2 mol equiv. of *N*-(4-acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine.† The ruthenium(II) complex **2** was synthesized by complexation with *cis*-Ru(bpy)$_2$Cl$_2$ and subsequent treatment with NH$_4$PF$_6$. Chemical oxidation of complex **2** was achieved with 2 mol equiv. of Ag$_2$O to give the corresponding oxidized complex **3** (Scheme 1). Furthermore, **3** could be reduced to **2** on treatment with $N_2H_4 \cdot H_2O$ at room temperature for 3 h under argon. These complexes were identified by spectral data and cyclic voltammetry.‡ For example, **3** exhibited a CT band at *ca.* 400–600 nm together with an MLCT band, in contrast to the observation of only the MLCT band for **2**.

The redox properties were studied by cyclic voltammetry. The redox waves were assigned by comparison with those of the corresponding complexes **4** and **5** bearing anilino and anilino-anilino groups, respectively (Table 1). The electrochemical behavior of complex **2** in acetonitrile is explained by the redox processes $D^0 \rightarrow D^+ \rightarrow D^{2+} \rightarrow D^{4+}$ of the quinonediimine moieties as shown in Scheme 2. The redox behavior of the ruthenium bipyridyl moiety was similar to that for complexes **4** or **5**. A multiredox system has thus been achieved with complex **2**. It should be noted that the redox processes were found to depend on the solvent. The redox waves in DMF were different from those observed in acetonitrile, suggesting the redox processes $D^0 \rightarrow D^{2+} \rightarrow D^{3+} \rightarrow D^{4+}$ in the former. Two quinonediimine moieties exhibited the same redox potential at each step in both solvents.

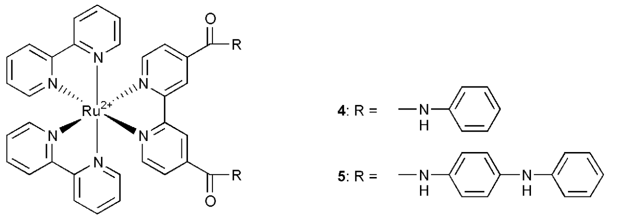


Scheme 1

The radical cationic species **6** could be generated by treatment of **2** with **3** in the presence of a proton source (HClO$_4$) with the appearance of a broad absorption (600–1100 nm) in the UV–VIS–NIR spectrum.§ EPR spectroscopy also supported the formation of **6** (g = 2.004, A_N = 6.7 G, $A_{H(CH)}$ = 1.6 G, $A_{H(NH)}$ = 3.4 G). These findings are consistent with the reported redox behavior of *N*,*N*′-diphenyl-1,4-benzoquinonediimine and *N*,*N*′-diphenyl-1,4-phenylenediamine.[7] The above-mentioned solvent effect might be due to the difference in equilibrium between the diprotonated quionediimine and corresponding reduced species, and the radical cationic species.

In the emission spectrum of complex **2** excited at 477 nm, almost complete quenching was observed in acetonitrile (Fig.

Table 1 Electrochemical data for **2**, **4** and **5**[a]



	$E_{1/2}$/V (*vs.* Fc/Fc$^+$)					
Complex	bpy$^{-/0}$	D$^{0/+}$	D$^{+/2+}$	D$^{2+/3+}$	D$^{3+/4+}$	Ru$^{2+/3+}$
2	−1.50	−0.01	+0.38	+0.93[c]	+0.93[c]	+0.93[c]
2[b]	−1.50	−0.10[c]	−0.10[c]	+0.63	+0.93[c]	+0.93[c]
4	−1.48					+0.94
5	−1.49	+0.48	+0.88			+0.94

[a] [Complex] = 0.25 mM; solv, MeCN. Recorded with NBu$_4$PF$_6$ as electrolyte (0.1 M). Potentials were obtained by cyclic voltammetry with a scan rate of 100 mV s^{-1}. D: π-conjugated pendant group. [b] Solv, DMF. [c] Observed simultaneously.

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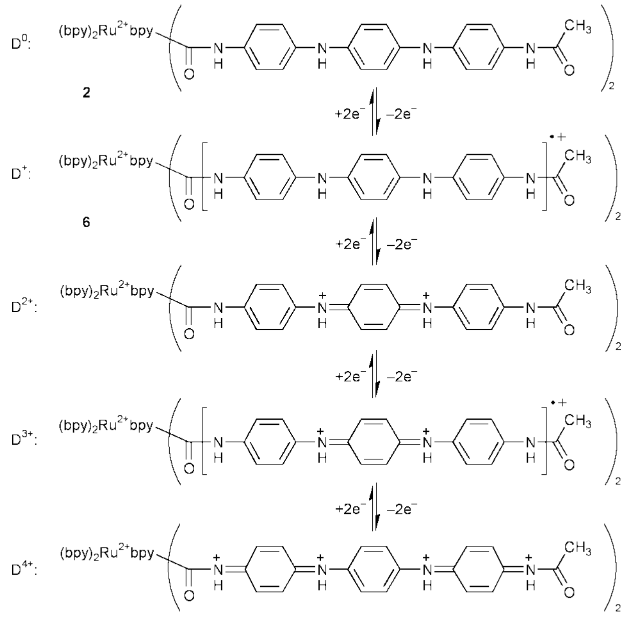

Scheme 2

1). Such quenching was not observed with **4**, indicating that the π-conjugated chain of **2** contributes to the quenching. An efficient photoinduced electron transfer is likely to operate in complex **2**, where the reduced form of the π-conjugated pendant groups serves as an electron donor. Use of the oxidized form **3** also resulted in a quenched spectrum upon excitation at 477 nm. Taking the reported electron-transfer mechanism of complexes bearing viologen or benzoquinone moiety into account,[1,2] this result might be explained by electron transfer in a direction opposite to that of **2**. A much less effective quenching of ruthenium(II) complex **4** with *N*,*N*′-bis(4-acetylaminophenyl)-1,4-phenylenediamine or *N*,*N*′-bis(4-acetylaminophenyl)-1,4-benzoquinonediimine was observed intermolecularly, indicating that the quenching process for both **2** and **3** occurs intramolecularly. Such intramolecular quenching processes are considered to be thermodynamically feasible.

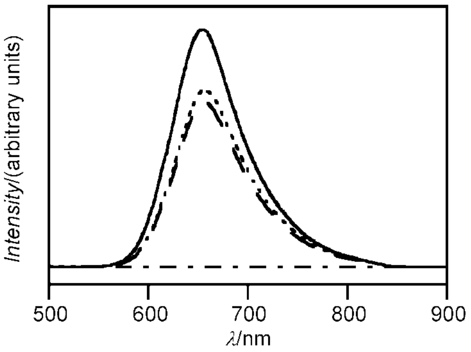

Fig. 1 Emission spectra of **2** or **3** (-·-), **4** (—), **4** with 2.0 mol equiv. of *N*,*N*′-bis(4-acetylaminophenyl)-1,4-phenylenediamine (····), and **4** with 2.0 mol equiv. of *N*,*N*′-bis(4-acetylaminophenyl)-1,4-benzoquinonediimine (- -). [Complex] = 2.0 × 10^{-5} M; solv, MeCN, λ_{exc} = 477 nm.

In conclusion, we have described a versatile and efficient redox-switching system with variable oxidation state of the π-conjugated pendant moieties. Further investigation on the electron-transfer mechanism and molecular recognition is now in progress.

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Notes and references

† The acid chloride derivative prepared by treatment of 2,2′-bipyridine-4,4′-dicarboxylic acid (122 mg, 0.50 mmol) with SOCl$_2$ (238 mg, 2.0 mmol) was dissolved in DMF (40 mL) and added dropwise over 2 h to a solution of *N*-(4-acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine[5] (332 mg 1.0 mmol), 4-dimethylaminopyridine (12 mg, 0.10 mmol) and Et$_3$N (0.50 mL) in DMF (20 mL) at 0 °C. After stirring at room temp. for 24 h, work-up gave the pure bipyridyl ligand **1** (342 mg, 0.39 mmol, 78%). **1**: IR (KBr) 3408, 3305, 3265, 1652 cm^{-1}; δ_H(300 MHz, DMSO-d$_6$) 10.51 (s, 2H), 9.69 (s, 2H), 8.94 (d, 2H, *J* 5.2 Hz), 8.91 (d, 2H, *J* 1.6 Hz), 7.97 (dd, 2H, *J* 5.2, 1.6 Hz), 7.87 (s, 2H), 7.76 (s, 2H), 7.62 (d, 4H, *J* 9.0 Hz), 7.39 (d, 4H, *J* 8.8 Hz), 7.04–6.90 (m, 16H), 1.99 (s, 6H); MS (FAB) *m*/*z* 872 M$^+$.

‡ **2**: IR (KBr) 3405, 3291, 1654 cm^{-1}; δ_H(600 MHz, DMSO-d$_6$) 10.55 (s, 2H), 9.67 (s, 2H), 9.34 (s, 2H), 8.88–8.87 (m, 4H), 8.23–8.20 (m, 4H), 7.96–7.95 (m, 4H), 7.89 (s, 2H), 7.81–7.75 (m, 4H), 7.76 (s, 2H), 7.59–7.54 (m, 4H), 7.54 (d, 4H, *J* 8.9 Hz), 7.38 (d, 4H, *J* 8.9 Hz), 7.01–6.96 (m, 12H), 6.91 (d, 4H, *J* 8.9 Hz), 1.99 (s, 6H); MS (FAB) *m*/*z* 1431 (M − PF$_6$)$^+$; UV–VIS (MeCN) λ_{abs}/nm (log ε) 289 (5.08) 304 (5.04) 477 (4.42). **3**: IR (KBr) 3404, 1669, 1529 cm^{-1}; UV–VIS (MeCN) λ_{abs}/nm (log ε) 288 (5.00) 482 (4.64).

§ UV–VIS–NIR (MeCN) λ_{abs}/nm (log ε) 288 (4.96) 405 (4.72) 847 (4.44).

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