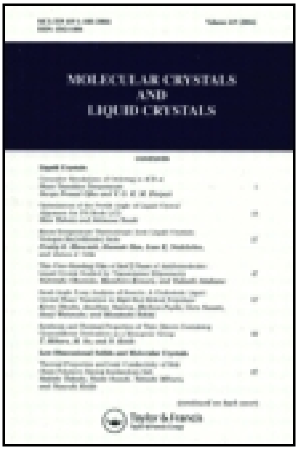

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Synthesis and Physical Properties of a π-Conjugated Ruthenium(II) Dinuclear Complex Involving an Azobenzene-Bridged Bis(terpyridine) Ligand

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A novel π-conjugated Ru(II) dinuclear complex containing a new azobenzene-bridged bis(terpyridine) ligand was synthesized and its photochemical and electrochemical properties were investigated. The ligand underwent reversible *trans-cis* photoisomerization, whereas the Ru complex did not show such photoisomerization behavior. Cyclic voltammetry of the complex displayed a reversible one-step $2e^-$ oxidation wave due to Ru(III)Ru(III)/Ru(II)Ru(II) and four $1e^-$ reduction waves indicating the formation of mixed-valence states when the electrons are accumulated at the ligand-based orbitals.

Keywords: azobenzene; ruthenium; photoisomerization; electrochemistry; terpyridine; dinuclear complex

INTRODUCTION

It is well known that oligonuclear polypyridyl complexes, in which two terpyridine units are connected via a π-conjugated spacer, show peculiar photochemical and electrochemical properties.[1,2] The azo group has the characteristic of photoisomerization,[3] and its nature of π-conjugation has a capability to mediate electronic interaction between metal centers when it is inserted between metal complex units.[4,5] Thus the oligonuclear complexes containing the azo-bridge will be useful substances for constructing the molecular switching system[6] driven not only by photoirradiation but also electrochemical input. In this study, we synthesized a new azobenzene-bridged bis(terpyridine) ligand, tpy-AB-tpy and its Ru(II) dinuclear complex, and investigated their photochemical and electrochemical properties.

EXPERIMENTAL

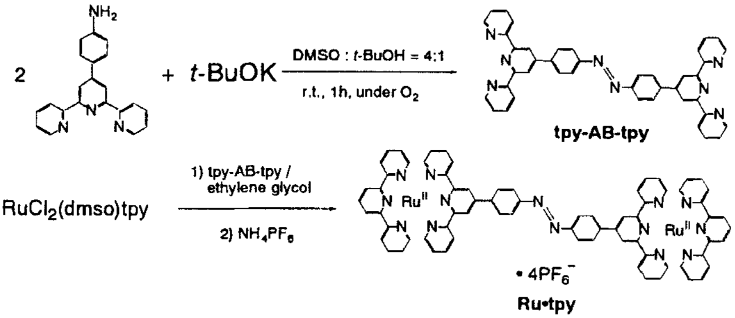
1. Materials and Apparatus

All the solvents and reagents commercially available were of guaranteed grade and used as received. 4'-(4-Anilino)-2,2':6',2"-terpyridine was prepared by a modified method[*] of that given in the literature.[7] Dichloro(dimethylsulfoxide)(2,2':6',2"-terpyridine)ruthenium(II) was prepared according to the literature.[8]

^{1}H-NMR and UV-Vis absorption spectra were recorded with a JEOL EX270 and a JASCO V-570 UV-Vis-NIR spectrometer, respectively. Photoirradiation was carried out with a 500 W super high pressure mercury lamp 500D-0 (Ushio) and 360-nm or 450-nm light was isolated with a Toshiba UV-D35 or KL-45 filter, respectively.

2. Synthetic Procedure

SCHEME 1



tpy-AB-tpy

4'-(4-Anilino)-2,2':6',2"-terpyridine (1.00 g, 3.08 mmol) was dissolved in DMSO/*t*-BuOH (25 ml, 4:1 v/v), and potassium *t*-butoxide (0.69 g, 6.2 mmol) was added. Oxygen gas was slowly bubbled into the solution with stirring at room temperature for 1 h. The precipitate was filtered off, and washed with CH_3OH and $CHCl_3$. Tpy-AB-tpy was obtained as an orange precipitate by Soxhlet extraction with $CHCl_3$;

[*] 4'-(4-Acetamido)-2,2':6',2"-terpyridine was obtained by one-pot codensation of 2-acetylpyridne and 4-acetamidobenzaldehyde. The acetamido group was hydrorized to form 4'-(4-acetamido)-2,2':6',2"-terpyridine in a hot HBr solution.

yield 0.50g (50%). Anal. Calcd. for $C_{42}H_{28}N_8$: C, 78.24; H, 4.38; N, 17.38. Found: C, 76.70; H, 4.59; N, 17.13. ^{1}H-NMR ($CDCl_3$): δ 8.81 (s, 4H), 8.74 (d, 4H, J = 4.6 Hz), 8.68 (d, 4H, J = 8.2), 8.10-8.00 (m, 8H), 7.89 (td, 4H, J = 8.2, 1.4), 7.36 (ddd, 4H, J = 8.2, 4.6, 1.4). FAB MS m/z 645 $(M+H)^+$. Electronic spectrum ($CHCl_3$): 246 (log ε = 4.68), 280 (4.71), 358 (4.65), 450 (3.17) nm.

[tpyRu (tpy-AB-tpy)Rutpy]•$4PF_6$ (Ru•tpy)

An ethylene glycol solution of $RuCl_2$(dmso)tpy (0.054 g, 0.11 mmol) and tpy-AB-tpy (0.036 g, 0.055 mmol) was refluxed for 2 h. An excess amount of NH_4PF_6 in water (30 ml) was added into the filtrate. The precipitate was filtered off and recrystallized from acetone/$CHCl_3$. A reddish violet powder of Ru•tpy was obtained; yield 0.073g (68%). Anal. Calcd. for $C_{72}H_{50}F_{24}N_{14}P_4Ru_2 \cdot 3H_2O$: C, 44.41; H, 2.90; N, 10.07. Found: C, 44.55; H, 3.31; N, 10.17. ^{1}H-NMR(CD_3CN): δ 9.11 (d, 4H, J = 3.3 Hz), 8.78 (d, 4H, J = 8.3), 8.70 (d, 4H, J = 8.3), 8.54 - 8.38 (m, 14H), 8.02-7.92 (m, 8H), 7.46 (dd, 4H, J = 5.4, 1.0), 7.39 (d, 4H, J = 4.9, 0.6), 7.23-7.18 (m, 8H). ESI MS m/z = 802.2 ($C_{72}H_{50}N_{14}P_2F_{12}Ru_2^{2+}$ requires 801.7), 486.6 ($C_{72}H_{50}N_{14}PF_6Ru_2^{3+}$ requires 486.1). 328.6 ($C_{72}H_{50}N_{14}Ru_2^{4+}$ requires 328.4). Electronic spectrum (CH_3CN): 272 (log ε = 4.95), 308 (5.12), 324 (shoulder, 4.95), 346 (shoulder, 4.67), 490 (4.80) nm.

3. Measurement of Cyclic Voltammetry

Cyclic voltammetry was carried out in a standard one-compartment cell equipped with a glassy-carbon disk (5 mmϕ) working electrode, a platinum–wire counter electrode and an Ag/Ag^+ reference electrode, under an argon atmosphere with a BAS CV-50W voltammetric analyzer.

RESULTS AND DISCUSSION

1. Photochemistry

As for tpy-AB-tpy, the absorption bands due to the N=N moiety were observed at 358 nm (π-π* transition) and ca. 450 nm (n-π* transition). *Trans*-to-*cis* isomerization was observed upon 360-nm light irradiation of tpy-AB-tpy in $CHCl_3$ under N_2. The *cis*-form thus generated was facilely reisomerized into the *trans*-form by irradiation with a 450-nm light. The recovery occurred slowly even at room temperature in the dark.

In the UV-Vis absorption spectrum of Ru•tpy, a band due to the π-π* transition of the azobenzene moiety appeared as a weak shoulder band around 360 nm, which was not as obvious as that of tpy-AB-tpy. The intensity of the MLCT band for Ru•tpy (at 490 nm) was stronger than for $[Ru(tpy)_2]^{2+}$,[9] and compatible to $[Ru(tpy)(ph\text{-}tpy)]^{2+}$,[9] where ph-tpy denotes 4'-phenyl-2,2';6',2''-terpyridine (Figure 1, inset), suggesting that the two phenyl rings of tpy-AB-tpy have considerable electronic communication with the Ru centers. Ru•PF_6 showed the emission with λ_{em} = 635 nm (λ_{ex} = 487 nm), in ethanol – methanol (4:1 v/v) glasses at 77K. Upon irradiation at 360 nm in CH_3CN, no significant spectral change was observed. We deduce that the suppression of the photoisomerization of tpy-AB-tpy by the complexation is caused by the contribution of the bypassed energy transfer relating to the Ru d-orbital(s) in the deexcitation for the photoisomerization.

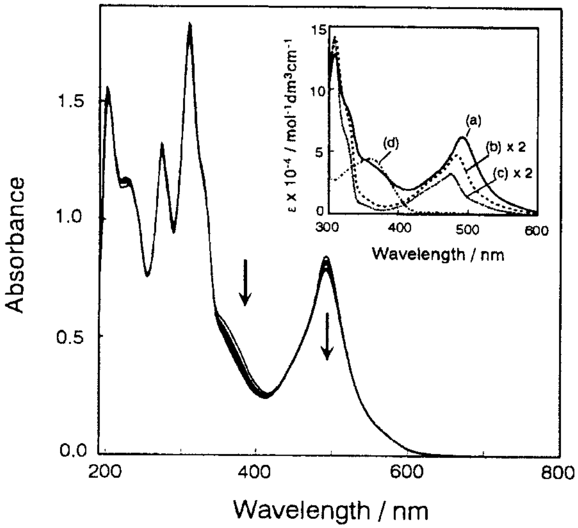


FIGURE 1 UV-Vis spectral change of Ru•tpy in CH_3CN (1.3×10^{-4} mol dm^{-3}) upon irradiation with a 360-nm light. Inset: the specra of Ru•tpy(a), $[Ru(tpy)(ph\text{-}tpy)]^{2+}$ (b), $[Ru(tpy)_2]^{2+}$ (c), and tpy-AB-tpy (d).

2. Electrochemistry

Ru•tpy showed reversible redox processes (Figure 2) like other Ru dinuclear complexes;[7] oxidation due to the Ru(II)/Ru(III) couple and reduction processes where the transferred electrons are localized not at the Ru center but at the either of the terpyridine units of the ligands. The oxidation process is observed as one-step 2e$^-$ reaction at $E^{0'}$ = +0.94 V *vs.* Ag/Ag$^+$, indicating scarce formation of the Ru(II)Ru(III) mixed-valence state. On the contrary, the reduction process is made of four-step 1e$^-$ reactions as can be written in Scheme 2, since the terpyridine bound to electron-withdrawing azobenzene group should be more easily reduced compared to the unsubstituted terpyridine.

SCHEME 2

	$E^{0'}$(V *vs.* Ag/Ag$^+$)
tpyRu^{II}(tpy-AB-tpy)Ru^{II}tpy	
	-1.26
tpyRu^{II}(tpy-AB-tpy)$^-$Ru^{II}tpy	
	-1.39
tpyRu^{II}(tpy-AB-tpy)$^{2-}$Ru^{II}tpy	
	ca. -1.7
tpyRu^{II}(tpy-AB-tpy)$^{2-}$Ru^{II}(tpy)$^-$	
	ca. -1.9
(tpy)$^-$Ru^{II}(tpy-AB-tpy)$^{2-}$Ru^{II}(tpy)$^-$	

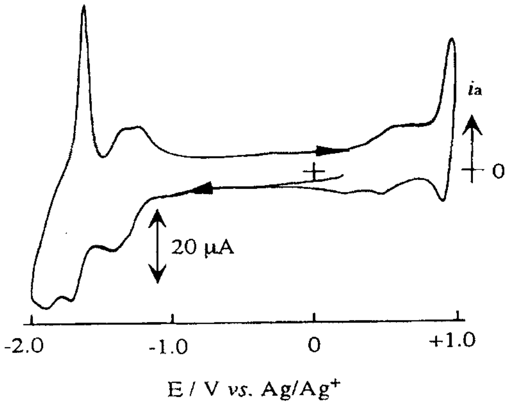


FIGURE 2 Cyclic voltammogram of Ru•tpy in 0.1 M Bu_4NBF_4 – MeCN (scan rate 100 mV s^{-1}).

It should be noted that the second reduction process at ca. −1.7 V and

−1.9 V was obscured probably by the surface adsorption of the reduced species. The formation of two mixed-valence states, tpyRu^{II}(tpy-AB-tpy)$^-$Ru^{II}tpy and tpyRu^{II}(tpy-AB-tpy)$^{2-}$Ru^{II}(tpy)$^-$ indicates the existence of strong electronic interaction between the reduced forms of complex units via the tpy-AB-tpy ligand.

CONCLUSION

We have synthesized a new azobenzene-bridged bis(terpyridine) ligand, tpy-AB-tpy, and its Ru dinuclear complex, Ru•tpy. Tpy-AB-tpy shows reversible *trans-cis* isomerizaton, similarly to azobenzene derivatives. On the other hand, the photoisomerization is suppressed by the bypassed energy transfer relating to the Ru d-orbital(s) in the deexcitation for the photoisomerization. The cyclic voltammogram shows a reversible 2e$^-$ oxidation wave due to Ru(III)Ru(III)/ Ru(II)Ru(II) and two pairs of 1e$^-$ reduction waves. This indicates that Ru(tpy)$_2$ fragments electrochemically interact each other in their reduced forms via the tpy-AB-tpy ligand.

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