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SYNTHESIS AND PHOTOCHEMICAL PROPERTIES OF COVALENTLY-LINKED DIMERS OF RUTHENIUM(II) TRIS (BIPYRIDINE) COMPLEX: COMPARISON WITH Ru(II)(bpy)$_2$ (POLY-4-METHYL-4'-VINYLBIPYRIDINE)

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ABSTRACT

Covalently linked dimers of Ru(bpy)$_3{}^{2+}$ (**3** and **4**) connected by two or three carbon atoms were synthesized as models for Ru(bpy)$_3{}^{2+}$-containing vinyl polymer (**1**). The luminescence properties of **3** and **4** were compared with those of its component monomer, 4,4'-dimethyl-2,2'-bipyridine-bis(2,2'-bipyridine)ruthenium(II) complex (**2**). In excited **3** and **4**, intramolecular interaction leading to enhanced quenching was not observed. Electron-transfer quenching of the excited dimer with methylviologen (MV^{2+}) and the zwitterionic viologen, 1,1'-bis(3-sulfopropyl)-4,4'-bipyridinium (SPV), was studied and compared with that of **1** and **2**. The low quenching efficiency in **1**, **3**, and **4** systems can be ascribed to the steric hindrance of unexcited ruthenium complex. Energy migration between ruthenium complexes in the excited **1**, **3**, and **4** can be ruled out from the kinetic evidence.

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INTRODUCTION

Molecular assemblies consisting of polypyridine complexes of transition metals are of interest in view of systems capable of photochemical energy conversion analogous to photosynthesis [1, 2]. A possible use of these materials is to control photochemical processes in which optical excitation is followed by a spatially directed energy or electron migration along the sequence of chromophores [3]. We have studied photochemical and photophysical properties of tris(bipyridine)ruthenium(II)-containing vinyl polymer **1** [4-6]. The luminescence properties of **1** showed close resemblance to those of its component monomer **2**, that is, 4,4′-dimethyl-2,2′-bipyridine-bis(bipyridine)ruthenium(II) complex. In contrast to polyvinylaromatics [7], there was no evidence for energy migration and electron exchange between ruthenium complexes on the polymer chain [5, 6]. In order to gain a better understanding of events which take place in the polymer, it is necessary to work on tris(bipyridine)-ruthenium complex dimer [8]. Here, we wish to report synthesis of ruthenium complex dimers (**3** and **4**) and their photophysical and photochemical properties. The electron-transfer quenching of excited **3** and **4** with methylviologen (MV^{2+}) and 1,1′-bis(3-sulfopropyl)-4,4′-bipyridinium (SPV) was studied and compared with that of excited **1** and **2** (see page 1265).

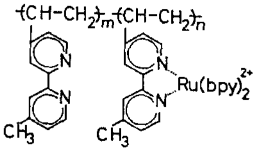
EXPERIMENTAL

Materials

The syntheses of **3** and **4** are outlined in Scheme 1. Compounds **3** (*n* = 2), **3** (*n* = 3), **4**, **5**, **6**, **7**, **10**, **11**, and **12** were newly synthesized, while **8** has been known and synthesized by a different procedure [10].

4-Methyl-2,2′-bipyridine-4′-carboxaldehyde (5)

A mixture of 4,4′-dimethyl-2,2′-bipyridine (12.5 g, 68 mmol) and selenium dioxide (7.52 g, 68 mmol) in 120 mL Diglyme was stirred at 130-135°C for 6 h. The reaction mixture was dissolved in 1 L hot water and filtered to remove selenium metal. The filtrate was adjusted to pH 9-10 with 10% NaOH and extracted four times with 300 mL $CHCl_3$ portions. The extract was dried ($MgSO_4$) and evaporated to give a pale yellow solid. Column chromatography on silica gel (ethyl acetate) afforded a white solid **5** (5.3 g, 40%), mp 135-136°C: ^1H NMR ($CDCl_3$) δ2.5 (s, 3H), 7.0-9.0 (m, 6H), 10.3 (s, 1H); IR (Nujol) 1710 cm^{-1}.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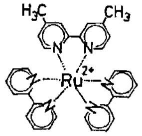
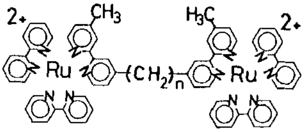
N
N
N
N
Ru(bpy)2 2+
CH3
CH3

1


H3C
CH3
N
N
Ru 2+

2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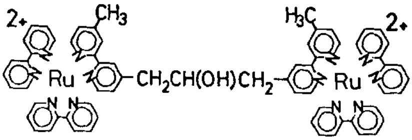
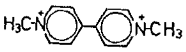
CH3
H3C
2+
Ru
(CH2)n
Ru
N N
N N

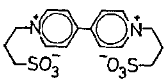
3


2+
CH3
H3C
2+
Ru
CH2CH(OH)CH2
Ru
N N
N N

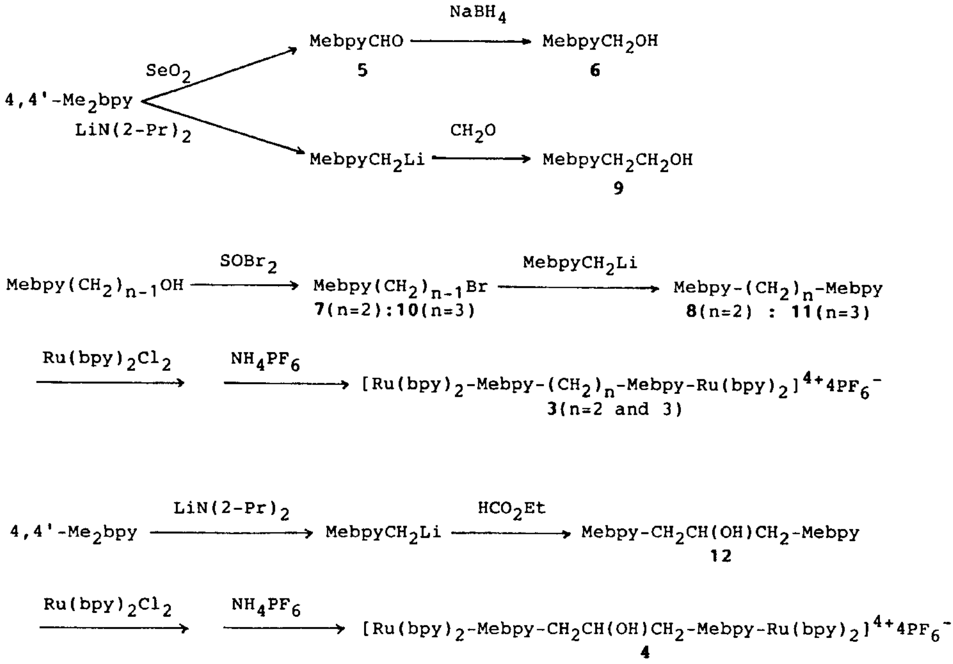
4


H3C-N+
N+-CH3

MV^{2+}


N+
N+
SO3-
-O3S

SPV



SCHEME 1. Preparation of dimers of ruthenium(II) tris(bipyridine) complex.

Analysis. Calculated for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.74; H, 5.11; N, 14.03.

4-Hydroxymethyl-4′-methyl-2,2′-bipyridine (6)

A solution of **5** (5.3 g, 27 mmol) and sodium borohydride (3 g, 79 mmol) in 350 mL anhydrous ethanol was stirred at room temperature for 1.5 h. Water (300 mL) was then added dropwise, and the mixture was stirred at room temperature overnight. The solution was extracted four times with 300 mL $CHCl_3$ portions. The extract was dried ($MgSO_4$) and evaporated to give a white solid. Recrystallization from ethanol provided 4.5 g (84%) of **6**, mp 124-125°C: ^1H NMR ($CDCl_3$) δ2.4 (s, 3H), 3.9-4.6 (s, 1H), 4.7 (s, 2H), 7.0-8.6 (m, 6H); IR (Nujol) 3200 cm^{-1}.

Analysis. Calculated for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.27; H, 6.08; N, 13.98.

4-Bromomethyl-4′-methyl-2,2′-bipyridine (7)

A mixture of **6** (2.0 g, 10 mmol) and thionyl bromide (5 mL, 63 mmol) in 25 mL CH_2Cl_2 was stirred at room temperature for 3 h under a flow of nitrogen gas. Water (200 mL) was added. The reaction mixture was neutralized (pH 8-9) with a saturated Na_2CO_3 solution and extracted with 500 mL CH_2Cl_2. After the extract was dried ($MgSO_4$) and evaporated below room temperature, the crude product was chromatographed on a silica gel column by eluting with ethyl acetate/CH_2Cl_2 (3:2) to give 0.78 g (30%) of white crystals of **7**, mp 76-77°C: ^1H NMR ($CDCl_3$) δ2.4 (s, 3H), 4.5 (s, 2H), 7.0-8.8 (m, 6H).

Analysis. Calculated for $C_{12}H_{11}N_2Br$; c, 54.77; H, 4.21; N, 10.65. Found: C, 54.48; H, 4.21; N, 10.56.

1,2-Bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane (8)

To a solution of 4,4′-dimethyl-2,2′-bipyridine (3.4 g, 18 mmol) in 200 mL TFH, lithium diisopropylamide (12 mmol) in THF (10 mL) was added at 0°C under argon and stirred for 1.5 h. A solution of 7 (2.0 g, 7.6 mmol) in 70 mL THF was then added dropwise at room temperature, and it was stirred for 1 h. The reaction was quenched with 10 mL methanol. The reaction mixture was diluted with 100 mL water and extracted with 1 L ether. The extract was dried ($MgSO_4$) and evaporated. The residue was placed on a silica gel column and eluted with a gradient mixture of ethyl acetate/CH_2Cl_2 from 1:9 to 3:1 to remove 4,4′-dimethyl-2,2′- bipyridine and unidentified by-products, and with methanol to provide a white solid of **8**. Recrystallization from ethanol yielded 1.4 g (50%) of **8**, mp 198-199°C: ^1H NMR ($CDCl_3$) δ2.5 (s, 6H), 3.2 (s, 4H), 7.0-9.0 (m, 6H).

Analysis. Calculated for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.66; H, 6.05; H, 15.23.

4-Bromoethyl-4′-methyl-2,2′-bipyridine (10)

4-Hydroxyethyl-4′-methyl-2,2′-bipyridine **9** was prepared as described elsewhere [4]. Using **9** (3.0 g, 14 mmol) and thionyl bromide (7.5 mL, 95 mmol) as the starting materials, the reaction was worked up by the procedure described in the preparation of 7, providing 1.8 g (46%) of **10** as a clear oil: ^1H NMR ($CDCl_3$) δ2.4 (s, 3H), 3.2 (t, 2H), 3.6 (t, 2H), 7.0-8.7 (m, 6H).

Analysis. Calculated for $C_{13}H_{13}N_2Br$: C, 56.52; H, 4.71; N, 10.07. Found: C, 56.52; H, 4.82; N, 10.15.

1,3-Bis(4′-methyl-2,2′-bipyridyl-4-yl)propane (11)

This was prepared from **10** (1.3 g, 5 mmol) by the procedure described in the preparation of **8**. 4-Methyl-4′-vinyl-2,2′-bipyridine (0.3 g) was obtained as a by-product from the early eluates. Yield of **11** was 1.2 g (63%), mp 128°C: ^{1}H NMR ($CDCl_3$) δ2.1 (q, 2H), 2.4 (s, 6H), 2.8 (t, 4H), 7.0-8.7 (m, 12H).

Analysis. Calculated for $C_{25}H_{24}N_4$: C, 70.04; H, 6.32; N, 14.64. Found: C, 78.71; H, 6.41; N, 14.61.

1,3-Bis(4′-methyl-2,2′-bipyridyl-4-yl)-2-hydroxypropane (12)

Ethyl formate (0.88 mL, 12 mmol) was added dropwise to a solution of monolithiated 4,4′-dimethyl-2,2′-bipyridine (30 mmol) in 150 mL THF at room temperature and stirred overnight. The mixture was quenched with 150 mL water, neutralized (pH 8-9) with 10 vol% methanolic HCl, and extracted four times with 100 mL $CHCl_3$ portions. The extracts was dried ($MgSO_4$) and evaporated to give a brownish-yellow solid. Purification of the crude product was achieved through several recrystallizations from methanol to provide a white solid **12** in a yield of 20%, mp 159-160°C. ^{1}H NMR ($CDCl_3$) δ2.45 (s, 6H), 2.93 (dd, 4H), 4.33 (m, 1H), 7.12-8.54 (m, 12H), m/e 396.

Analysis. Calculated for $C_{25}H_{24}NO$: C, 75.73; H, 6.10; N, 14.13. Found: C, 75.93; H, 6.12; N, 13.97.

Preparation of Dimers of Polypyridine Ruthenium(II) Complex [3 (*n* = 2), 3 (*n* = 3), and 4]

Complexes **3** (*n* = 2), **3** (*n* = 3), and **4** were all prepared in the same manner except for the dimer ligand used. A solution of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (560 mg, 1.1 mmol) and the appropriate dimer ligand (i.e., **8**, **11**, or **12**, 0.35 mmol) in 30 mL methanol was refluxed for 24 h. The solution was condensed to 5 mL, and the solid residues were filtered off. The solution was subjected to chromatography on Sephadex LH-20 with a methanol eluent. The middle portion of the cherry-red band was collected and evaporated to dryness to afford a ruthenium(II) complex as the Cl^- salt. The PF_6 salt was obtained by the following procedure. To a solution of the ruthenium(II) complex (Cl^- salt, 100 mg) in 10 mL water was added slowly a solution of NH_4PF_6 (300 mg) in water. The precipitate was collected by centrifugation, rinsed several times with water, and dried *in vacuo*.

Analysis. Calculated for $Ru_2C_{64}F_{24}N_{12}P_4 \cdot 3H_2O$ [**3** ($n = 2$) (PF_6)] : C, 42.07; H, 3.31; N, 9.20. Found: C, 42.14; H, 3.29; N, 9.07. Calculated for $Ru_2C_{65}H_{56}F_{24}N_{12}P_4 \cdot 2H_2O$ [**3** ($n = 3$) (PF_6)] : C, 42.82; H, 3.32; N, 9.22. Found: C, 42.60; H, 3.31; N, 9.22. Calculated for $Ru_2C_{65}H_{56}F_{24}N_{12}OP_4 \cdot 2H_2O$ [**4** (PF_6)] : C, 42.44; H, 3.29; N, 9.14. Found: C, 42.26; H, 3.37; N, 9.00.

Measurements

Absorption spectra were recorded on a Hitachi 124 spectrophotometer. Luminescence spectra were taken with a Shimadzu RF-502A spectrofluorimeter. The measurement of luminescent lifetime was performed with a Blumlein-type nitrogen laser system [4] and a time-correlated single-photon counting method [9]. Electrochemical measurements were performed in a conventional single-compartment cell equipped with a glassy-carbon working electrode and a saturated calomel electrode as a reference electrode (SCE). All measurements were obtained using a NF function generator FG-12113 and a Hokuto potentiostat HA-301 at scan rate 1.9-0.2 V/s. The sample solutions (1 m*M*) were deaerated by bubbling with argon gas.

RESULTS AND DISCUSSION

The electronic and redox properties of **3** and **4** in the ground state were compared with those of **2** (Table 1). Redox potentials in acetonitrile were measured by cyclic voltammetry using a glassy carbon electrode and tetrabutylammonium perchlorate as a supporting electrolyte. There were no substantial differences between **2** and dimers in values of the redox potentials and the peak separation at various stages. The peak-to-peak splitting for these waves is about 60 mV. This indicates that in **3** and **4**, successive one-electron oxidation and reduction processes take place. Electronic absorption spectra of dimers in water showed the same MLCT band at 455 nm as that of **2**. Comparison of redox and electronic properties of **3** and **4** with **2** provided no evidences for intramolecular interaction between ruthenium moieties in the ground state. It has been also suggested in polymer **1** [4].

The luminescence spectra showed maxima at 618 nm for **1**, 614 nm for **3** ($n = 2$), 616 nm for **3** ($n = 3$), and 615 nm for **4**, respectively. The luminescence intensities of dimers are in the range of 1.10-1.34 relative to **2**. The luminescence lifetime of **3** and **4** in a deaerated aqueous solution

TABLE 1. Photophysical and Electrochemical Properties of Ruthenium(II) Complexes

Ruthenium complex	Absorption λ_{max}, nm	λ_{max}, nm	Emission intensity[a]	Lifetime, ns	$E_{1/2}$[b], V	
					Ru^{3+}/Ru^{2+}	Ru^{2+}/Ru^{+}
1	455	618	1.40	660	1.21	- 1.38
2	455	613	1.00	490	1.21	- 1.38
3 (n = 2)	455	614	1.34	630	1.21	- 1.38
3 (n = 3)	455	616	1.10	520	1.21	- 1.38
4	455	615	1.24	481	1.21	- 1.38

[a] Relative value.
[b] Versus SCE.

was measured by the time-correlated single-photon counting method (excitation at 514.5 nm and instrumental width of 300 ps) and are listed in Table 1. **3** and **4** exhibited a single exponential decay similar to **4**. Careful examination on the fast decay process was carried out by observation of the decay at a short time range of 50 ns. There was no indication of the fast decay processes.

Concentration quenching is often observable in the concentrated solution of aromatic chromophores for which the quantum yield and lifetime of emission decrease in comparison with those in dilute solution [11]. When two aromatic chromophores are linked with a trimethylene chain, the intramolecular interaction leading to the excimer formation or other annihilation processes takes place in the excited state in a dilute solution [12]. In polyvinylaromatics, the interaction between excited and unexcited chromophores usually leads to formation of the excited state complex, such as an excimer, or opens a new channel to the nonradiative process. For instance, fluorescence lifetime and quantum yield of poly(9-vinylphenanthrene) are shorter and smaller than those of its monomer model, 9-ethylphenanthrene. By using 1,3-bis(9-phenanthryl)propane, this intramolecular interaction has been clearly demonstrated [13]. In ruthenium-containing vinyl polymers, luminescence behavior is rather different from that of polyvinylaromatics. Luminescence intensity and lifetime of the polymer are compared with those of $Ru(bpy)_3{}^{2+}$ in Table 2. The polymer containing 75 mol% of ruthenium(II) complex did not exhibit any evidence for intramolecular quenching. The high values of luminescence intensity and lifetime of the polymers containing lower contents (23 and 8%) of ruthenium complexes have been explained by the hydrophobic microenvironment of ruthenium complexes preventing quenching by water [4].

These findings on redox and luminescence properties of **1**, **3**, and **4** suggest that reactivities of ruthenium complexes in these molecular assemblies are similar or even higher than those of monomeric counterparts. Thus, **1**, **3**, and **4** offer a good prospect as photosensitizers. In this connection, the photosensitized reduction of viologen compounds such as methylviologen (MV^{2+}) and 1,1′-bis(3-sulfopropyl)-4,4′-bipyridinium (SPV) by ruthenium complexes **1**, **2**, **3**, and **4** was studied and discussed with Stern-Volmer (K_{SV}) and quenching rate (k_q) constants. Polymer **1** containing 75 mol% of ruthenium complex was used in this quenching study (Table 3).

In the case of cationic quencher MV^{2+}, small K_{SV} values of **1**, **3**, and **4** were obtained in pure water. Values of k_q for **1**, **3** ($n = 2$), **3** ($n = 3$), and **4** were 1.8×10^7, 1.9×10^7, 3.6×10^7, and 7.2×10^7 $M^{-1} \cdot s^{-1}$, respectively.

TABLE 2. Emission Intensity and Lifetime of Ru(II)(bpy)$_2$ (poly-4-methyl-4′-vinylbipyridine) (**1**)

Ru(II) complex[a]	Intensity[b]	Lifetime,[c] ns
$Ru(bpy)_3{}^{2+}$	1.00	660
1-75	1.17	660
1-71	1.07	660
1-50	1.43	720
1-32	1.43	690
1-23	1.48	740
1-8	1.76	940

[a] Ru(II) content in monomer unit (%).
[b] Relative intensity.
[c] Measured by a nitrogen laser system.

The k_q value for **2** was 1.3×10^8 $M^{-1} \cdot s^{-1}$. These values are much smaller than those with the neutral quencher SPV. This fact indicates that the electrostatic repulsion between ruthenium complexes and MV^{2+} is a dominant factor in suppression of the electron-transfer quenching. At higher ionic strength, such electrostatic interaction can be weakened. Therefore, we can expect the increase of k_q in the MV^{2+} system. In the presence of an inert salt (ionic strength: 0.5 *M*), K_{SV} and k_q values with MV^{2+} were in the order **2** > **4** > **3** ($n = 3$) > **3** ($n = 2$) > **1**. The same order and close values of k_q were also obtained with SPV. In spite of higher quantum yield of emission in **3** and **4**, the K_{SV} values were smaller than that of **2**. This fact can be explained as follows: a) Unexcited ruthenium complex of the excited **3** and **4** prevents sterically electron-transfer quenching; b) energy migration between ruthenium complexes of the excited **3** and **4** does not occur.

In conclusion, intramolecular interaction leading to ground-state quenching and even energy transfer between ruthenium complexes is unlikely because of the localized formulation of the excited states of **1**, **3**, and **4**. The low quenching efficiency in Polymer **1** systems can be ascribed to the low diffusion coefficient and the steric hindrance of unexcited ruthenium complexes which are located close to the reaction center.

TABLE 3. Photochemical Properties of Ruthenium(II) Complexes

Ruthenium complex	Emission lifetime, ns	MV^{2+}[a]		SPV[a]	
		K_{SV},[b] M^{-1}	k_q, 10^7 $M^{-1} \cdot s^{-1}$	K_{SV}, M^{-1}	k_q, 10^7 $M^{-1} \cdot s^{-1}$
1	660	12 (44)	1.8 (6.7)	88 (77)	13 (12)
2	490	63 (525)	13 (107)	670 (710)	138 (145)
3 (*n* = 2)	630	12 (261)	1.9 (41)	433 (530)	69 (84)
3 (*n* = 3)	520	19 (390)	3.6 (75)	595 (640)	114 (123)
4	481	35 (450)	7.2 (93)	626 (635)	130 (132)

[a] The values in parentheses indicate K_{SV} in 0.17 M Na_2SO_4 aqueous solution.

[b] Calculated from the initial slope.

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