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"Off-on-off" Fluorescence pH Switch of Three Trinuclear Ru^{II} Complexes Containing Imidazole Rings

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Abstract. Three tripodal ligands H_3L^{1-3} containing imidazole rings were synthesized by the reaction of 1,10-phenanthroline-5,6-dione with 1,3,5-tris[(3-formylphenoxy)methyl]benzene, 1,3,5-tris[(3-formylphenoxy)methyl]-2,4,6-trimethylbenzene, and 2,2',2"-tris[(3-formylphenoxy)ethyl]amine, respectively. Trinuclear Ru^{II} polypyridyl complexes $[(bpy)_6Ru_3H_3L^{1-3}](PF_6)_6$ were prepared by the condensation of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ with ligands H_3L^{1-3}. The pH effects on the UV/Vis absorption and fluorescence spectra of the three complexes were studied, and ground- and excited-state ionization constants of the three complexes were derived. The three complexes act as "off-on-off" fluorescence pH switch through protonation and deprotonation of imidazole ring with a maximum on-off ratio of 5 in buffer solution at room temperature.

Introduction

Ruthenium(II) polypyridyl complexes are currently widely investigated due to the rich electrochemical and photophysical properties and their potential applications in various molecular electronic devices.[1] Fluorescent sensors have drawn increasing attention for their use in fields as diverse as chemistry, biology, medical analysis, and environmental monitoring. Fluorescent sensors responding to external pH stimulations have received much attention in recent years due to their potential use in the measurement of pH and pCO_2 in biological and environmental systems. However, it is noticed that many pH sensor researches have primarily focused on organic molecules. Investigations of metal complexes have attracted less attention and their great potential as pH sensors has not been fully explored to date.[2] Ru^{II} polypyridyl complexes are good candidates as pH sensors, because of their sensitive photophysical and electrochemical properties.[3] The design of appropriate ligands is an important factor for a successful Ru^{II} polypyridyl pH sensor. In general, pyridine-containing ligands have relatively low-lying π* orbitals, and therefore act as good acceptors. In contrast, imidazole-containing ligands are poorer π acceptors and better π donors. Furthermore, imidazole-containing ligands have dissociative imino N–H protons, which can perturb the electronic properties of metal complexes through metal–ligand interactions. Protonation and deprotonation of metal complexes with imidazole rings can act as external trigger signals in molecular based switching devices. Although some Ru^{II} polypyridyl complexes containing imidazole fragments were synthesized, in most cases, these complexes with the imidazole rings coordinated to the metal atoms are non-emissive or weakly emissive and only display deprotonation processes.[4] Ru^{II} polypyridyl complexes with imidazole fragments that are not coordinated to the metal ion atoms are good emitters.

To the best of our knowledge, only several mono- and dinuclear Ru^{II} polypyridyl complexes of this type have been reported.[5] Herein, we report the synthesis and characterization of three novel trinuclear Ru^{II} polypyridyl complexes with imidazole rings uncoordinated to the Ru^{II} atoms, and the spectroscopic properties of the three complexes in response to pH changes.

Experimental Section

Materials: Solvents and raw materials were of analytical grade and were used as received. 1,3,5-Tris(bromomethyl)benzene, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene,[6] 1,10-phenanthroline-5,6-dione,[7] and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ [8] were synthesized according to literature procedures.

Physical Measurements: ^1H NMR spectra were performed with a Mercury Plus 300 spectrometer using TMS as internal standard. LC-MS spectra were recorded with a Bruker Daltonics Esquire 6000 mass spectrometer. Elemental analyses were taken with a Perkin–Elmer 240C analytical instrument. Absorption spectra were obtained with a Varian Cary-100 UV/Vis spectrophotometer. Emission spectra were obtained with a Hitachi F-4500 spectrophotometer.

Preparations

1,3,5-Tris[(3-formylphenoxy)methyl]benzene: A mixture of 3-hydroxybenzaldehyde (0.83 g, 6.80 mmol), 1,3,5-tris(bromomethyl)benzene

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(0.69 g, 1.95 mmol), and K_2CO_3 (1.13 g, 8.16 mmol) in DMF (30 mL) were heated to 80 °C for 24 h in a nitrogen atmosphere. After cooling to room temperature, the solution was diluted with water (300 mL). A colorless precipitate was formed and collected by filtration. This precipitate was purified by column chromatography on silica, eluting with CH_2Cl_2:CH_3CH_2OH (20:1) to afford the desired product as a colorless solid. Yield 391 mg (41.8 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 5.17 (s, 6 H), 7.24 (s, 3 H), 7.43–7.50 (m, 12 H), 9.97 (s, 3 H). **LC-MS**: *m/z* 481.0 $[M + H]^+$, 498.0 $(M + NH_4)^+$, 503.0 $[M + Na]^+$.

1,3,5-Tris[(3-formylphenoxy)methyl]-2,4,6-trimethylbenzene: The compound was prepared by the same procedure as described for 1,3,5-tris[(3-formylphenoxy)methyl]benzene, except 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.65 g, 1.64 mmol) was used instead of 1,3,5-tris(bromomethyl)benzene to react with 3-hydroxybenzaldehyde (0.71 g, 5.82 mmol). Yield 394 mg (46.0 %) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 2.47 (s, 9 H), 5.19 (s, 6 H), 7.27–7.30 (m, 3 H), 7.46–7.51 (m, 6 H), 7.56 (s, 3 H), 10.02 (s, 3 H). **LC-MS**: *m/z* 540.0 $(M + NH_4)^+$.

2,2',2"-Tris[(3-formylphenoxy)ethyl]amine: The compound was prepared by the same procedure as described for 1,3,5-tris[(3-formylphenoxy)methyl]benzene, except tris(2-chloroethyl)amine hydrochloride (0.76 g, 3.18 mmol) was used instead of 1,3,5-tris(bromomethyl)benzene to react with 3-hydroxybenzaldehyde (1.32 g, 10.82 mmol). Yield 325 mg (22.2 %) of a colorless ropy liquid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.21 (t, *J* = 5.7 Hz, 6 H), 4.17 (t, *J* = 5.1 Hz, 6 H), 7.14–7.16 (m, 3 H), 7.37–7.41 (m, 9 H), 9.95 (s, 3 H). **LC-MS**: *m/z* 462.2 $[M + H]^+$.

1,3,5-Tris{3-((1,10-phenanthroline-[5,6-d]imidazol-2-yl)phenoxy)methyl}benzene (H_3L^1): A mixture of 1,3,5-tris[(3-formylphenoxy)methyl]benzene (282 mg, 0.59 mmol), 1,10-phenanthroline-5,6-dione (456 mg, 2.17 mmol), and NH_4Ac (3.34 g, 43.38 mmol) in glacial acetic acid (45 mL) was heated to 130 °C for 3 h. A suspension formed during the heating process. The reaction mixture was filtered hot, subsequently washed with hot ethanol, hot DMF, and ethyl ether, respectively, to afford the desired product as a yellow solid. Yield 258 mg (41.8 %). **^{1}H NMR** (300 MHz, $[D_6]$DMSO): δ = 5.35 (s, 6 H), 7.21 (d, *J* = 7.8 Hz, 3 H), 7.52 (t, *J* = 8.1 Hz, 3 H), 7.72 (s, 3 H), 7.76 (s, 6 H), 7.88 (d, *J* = 7.8 Hz, 3 H), 7.99 (s, 3 H), 8.88 (t, *J* = 4.5 Hz, 6 H), 8.99 (s, 3 H), 9.00 (s, 3 H), 13.67 (s, 3 H). **LC-MS**: *m/z* 1051.6 $[M + H]^+$. Elemental anal. for $C_{66}H_{42}N_{12}O_3$: calcd. C 75.42, H 4.03, N 15.99 %; found: C 75.56, H 4.15, N 16.12 %.

1,3,5-Tris{3-((1,10-phenanthroline-[5,6-d]imidazol-2-yl)phenoxy)methyl}-2,4,6-trimethylbenzene (H_3L^2): H_3L^2 was prepared by the same procedure as described for H_3L^1, except 1,3,5-tris[(4-formylphenoxy)methyl]-2,4,6-trimethylbenzene (183 mg, 0.35 mmol) was used instead of 1,3,5-tris[(3-formylphenoxy)methyl]benzene to react with 1,10-phenanthroline-5,6-dione (273 mg, 1.30 mmol). Yield 175 mg (45.7 %) of a yellow solid. **^{1}H NMR** (400 MHz, $[D_6]$DMSO): δ = 2.39 (s, 9 H), 5.14 (s, 6 H), 7.22 (d, *J* = 7.8 Hz, 3 H), 7.59 (t, *J* = 7.8 Hz, 3 H), 7.82 (s, 6 H), 7.94 (s, 3 H), 7.97 (d, *J* = 4.8 Hz, 3 H), 8.95 (d, *J* = 7.8 Hz, 6 H), 9.02 (d, *J* = 3.9 Hz, 6 H), 13.79 (s, 3 H). **LC-MS**: *m/z* 1093.4 $[M + H]^+$. Elemental anal. for $C_{69}H_{48}N_{12}O_3$: calcd. C 75.81, H 4.43, N 15.38 %; found: C 75.96, H 4.56, N 15.49 %.

2,2',2"-Tris{3-((1,10-phenanthroline-[5,6-d]imidazol-2-yl)phenoxy)ethyl}amine (H_3L^3): H_3L^3 was prepared by the same procedure as described for H_3L^1, except 2,2',2"-tris[(3-formylphenoxy)ethyl]amine (216 mg, 0.47 mmol) was used instead of 1,3,5-tris[(3-formylphenoxy)methyl]benzene to react with 1,10-phenanthroline-5,6-dione (361 mg, 1.72 mmol). Yield 172 mg (35.6 %) of a yellow solid. **^{1}H NMR** (300 MHz, $[D_6]$DMSO): δ = 3.16 (s, 6 H), 4.22 (s, 6 H), 7.05 (d, *J* = 7.8 Hz, 3 H), 7.40 (t, *J* = 7.8 Hz, 3 H), 7.68 (dd, *J* = 7.8, 4.8 Hz, 6 H), 7.77 (d, *J* = 7.8 Hz, 3 H), 7.86 (s, 3 H), 8.74 (d, *J* = 7.8 Hz, 6 H), 8.91 (d, *J* = 2.1 Hz, 6 H). **LC-MS**: *m/z* 1032.6 $[M + H]^+$. Elemental anal. for $C_{63}H_{45}N_{13}O_3$: calcd. C 73.31, H 4.39, N 17.64 %; found: C 73.46, H 4.52, N 17.78 %.

$[(bpy)_6Ru_3H_3L^1](PF_6)_6$ $[RuH_3L^1](PF_6)_6$: A mixture of H_3L^1 (127 mg, 0.12 mmol) and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (226 mg, 0.43 mmol) in ethylene glycol (20 mL) was heated to 150 °C for 12 h in a nitrogen atmosphere. The color of the solution changed to red during the time. Afterwards, the solvent was evaporated under reduced pressure, the residue was purified twice by column chromatography on alumina eluting first with CH_3CN/ethanol (10:1) to remove impurities, additionally with CH_3CN/ethanol (5:1) to afford complex $[(bpy)_6Ru_3H_3L^1]Cl_6$, which was dissolved in a minimum amount of water followed by dropwise addition of saturated aqueous NH_4PF_6 until no more precipitate formed. The precipitate was purified by recrystallization from an acetonitrile-diethyl ether mixture (vapor diffusion method) to give a red solid. Yield 145 mg (37.9 %). **^{1}H NMR** (300 MHz, $[D_6]$DMSO): δ = 5.38 (s, 6 H), 7.28 (s, 3 H), 7.34 (t, *J* = 6.6 Hz, 6 H), 7.57–7.62 (m, 15 H), 7.76 (s, 3 H), 7.85 (d, *J* = 6.0 Hz, 6 H), 7.89–7.96 (m, 9 H), 8.04–8.05 (d, 9 H), 8.11 (t, *J* = 7.8 Hz, 6 H), 8.22 (t, *J* = 7.8 Hz, 6 H), 8.84 (d, *J* = 8.7 Hz, 6 H), 8.88 (d, *J* = 8.7 Hz, 6 H), 9.08 (d, *J* = 6.9 Hz, 6 H). **LC-MS**: *m/z* 1434.6 $(M - 2PF_6)^{2+}$, 1362.8 $(M - 3PF_6 - H)^{2+}$, 908.3 $(M - 3PF_6)^{3+}$, 860.3 $(M - 4PF_6 - H)^{3+}$, 810.5 $(M - 5PF_6 - 2\ H)^{3+}$, 609.1 $(M - 5PF_6 - H)^{4+}$, 572.6 $(M - 6PF_6 - 2\ H)^{4+}$. Elemental anal. for $C_{126}H_{90}F_{36}N_{24}O_3P_6Ru_3$: calcd. C 47.87, H 2.87, N 10.63 %; found: C 47.98, H 3.02, N 10.78 %.

$[(bpy)_6Ru_3H_3L^2](PF_6)_6$ $[RuH_3L^2](PF_6)_6$: $[RuH_3L^2](PF_6)_6$ was prepared by the same procedure as described for $[RuH_3L^1](PF_6)_6$, except H_3L^2 (113 mg, 0.10 mmol) was used instead of H_3L^1 to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (192 mg, 0.37 mmol) affording a red solid. Yield 152 mg (45.8 %). **^{1}H NMR** (300 MHz, $[D_6]$DMSO): δ = 2.52 (s, 9 H), 5.33 (s, 6 H), 7.33 (t, *J* = 6.3 Hz, 6 H), 7.56–7.58 (m, 15 H), 7.83 (d, *J* = 4.8 Hz, 12 H), 7.91 (s, 6 H), 8.01 (d, *J* = 8.1 Hz, 3 H), 8.05–8.10 (m, 9 H), 8.16–8.22 (m, 9 H), 8.82 (d, *J* = 8.7 Hz, 6 H), 8.86 (d, *J* = 8.7 Hz, 6 H), 9.05 (s, 6 H). **LC-MS**: *m/z* 777.5 $(M - 6PF_6 - 3\ H)^{3+}$, 656.6 $(M - 4PF_6)^{4+}$, 619.3 $(M - 5PF_6 - H)^{4+}$, 582.8 $(M - 6PF_6 - 2\ H)^{4+}$, 495.5 $(M - 5PF_6)^{5+}$, 466.8 $(M - 6PF_6 - H)^{5+}$, 389.4 $(M - 6PF_6)^{6+}$. Elemental anal. for $C_{129}H_{96}F_{36}N_{24}O_3P_6Ru_3$: calcd. C 48.37, H 3.02, N 10.49 %; found: C 48.52, H 3.13, N 10.63 %.

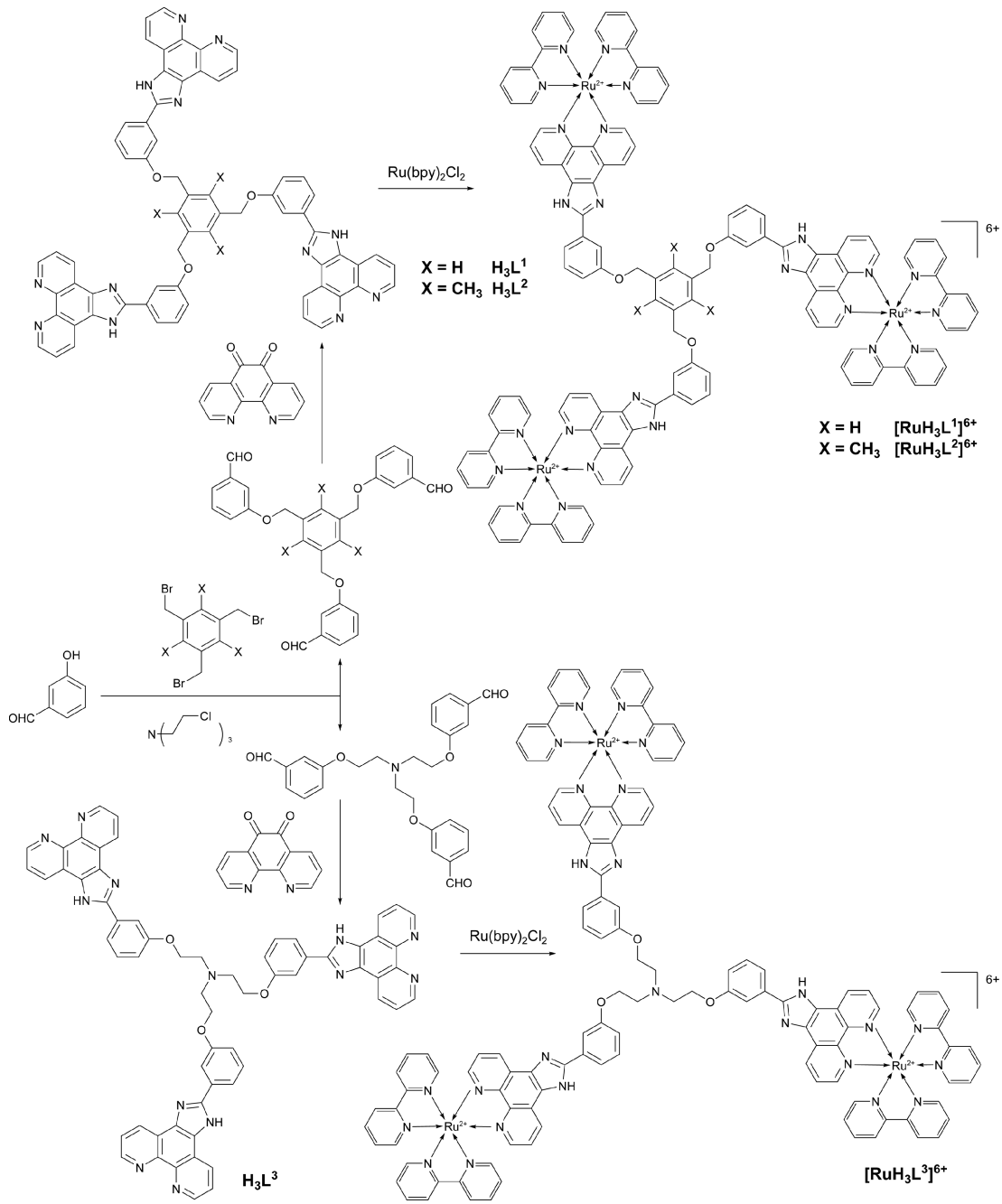
$[(bpy)_6Ru_3H_3L^3](PF_6)_6$ $[RuH_3L^3](PF_6)_6$: $[RuH_3L^3](PF_6)_6$ was prepared by the same procedure as described for $[RuH_3L^1](PF_6)_6$, except H_3L^3 (132 mg, 0.13 mmol) was used instead of H_3L^1 to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (239 mg, 0.46 mmol) affording a red solid. Yield 167 mg (41.5 %). **^{1}H NMR** (300 MHz, $[D_6]$DMSO): δ = 3.26 (s, 6 H), 4.34 (s, 6 H), 7.16 (d, *J* = 8.1 Hz, 3 H), 7.31–7.37 (m, 6 H), 7.47 (t, *J* = 7.8 Hz, 3 H), 7.55–7.67 (m, 15 H), 7.69 (t, *J* = 6.3 Hz, 3 H), 7.73–7.84 (m, 9 H), 7.91 (s, 3 H), 7.96–8.00 (m, 6 H), 8.09 (t, *J* = 7.5 Hz, 6 H), 8.20 (t, *J* = 7.8 Hz, 6 H), 8.82–8.88 (m, 18 H) ppm. **LC-MS**: *m/z* 903.6 $(M - 3PF_6)^{3+}$, 853.1 $(M - 4PF_6 - H)^{3+}$, 641.2 $(M - 4PF_6)^{4+}$, 604.1 $(M - 5PF_6 - H)^{4+}$, 567.3 $(M - 6PF_6 - 2\ H)^{4+}$, 483.5 $(M - 5PF_6)^{5+}$, 454.3 $(M - 6PF_6 - H)^{5+}$, 379.1 $(M - 6PF_6)^{6+}$. Elemental anal. for $C_{123}H_{93}F_{36}N_{25}O_3P_6Ru_3$: calcd. C 47.02, H 2.98, N 11.14 %; found: C 47.15, H 3.10, N 11.27 %.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and mass spectra of the ligands and corresponding Ru^{II} complexes are included.

Results and Discussion

Synthesis

An outline of the synthesis of ligands and corresponding Ru^{II} complexes is presented in Scheme 1. Ligands were synthesized on the basis of the method for imidazole ring preparation established by *Steck* et al.[9] H_3L^1, H_3L^2, and H_3L^3 were synthesized in good yield by the reaction of 1,10-phenanthroline-5,6-dione with 1,3,5-tris[(3-formylphenoxy)methyl]benzene, 1,3,5-tris[(4-formylphenoxy)methyl]-2,4,6-trimethylbenzene, and 2,2',2"-tris[(3-formylphenoxy)ethyl]amine, respectively, in refluxing glacial acetic acid at a molar ratio of 1:3. For each of the three ligands, the Ru^{II} complex was prepared by heating the starting materials $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and the respective ligand in ethylene glycol solution for 12 h in a nitrogen atmosphere under reflux. The resulting complexes were characterized by ^1H NMR spectroscopy, LC-mass spectrometry, and elemental analysis. The proton on the nitrogen atom of the imidazole resonates at δ = 13.7 for the free ligands H_3L^{1-3} as a broad singlet, but it is unobserved for the complexes $[Ru_3H_3L^{1-3}](PF_6)_6$ because of quickly exchange between the two nitrogen atoms of the imidazole ring.



Scheme 1. Synthesis of tripodal ligands H_3L^{1-3} and Ru^{II} complexes $[RuH_3L^{1-3}]^{6+}$.

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Spectroscopic Properties

Absorption spectra of the three complexes were studied in CH_3CN solution. Working concentration of all samples was 5×10^{-6} mol·L^{-1}. The spectra are shown in Figure 1 with the data summarized in Table 1. Assignments of the absorption bands are made on the basis of the well-documented optical transitions of some Ru^{II} polypyridyl complex analogs.[5] The absorption spectra of complexes $[RuH_3L^{1-3}]^{6+}$ comprise four regions, bands at around 286 and 240 nm are attributed to the intraligand $\pi \rightarrow \pi^*$ transitions centered on the bipyridine. At higher energy region around 326 nm, the spectra display one characteristic band of tripodal ligand, corresponding to $\pi(H_3L) \rightarrow \pi^*(H_3L)$. The lowest energy band at around 459 nm is attributed to MLCT transition and consists of overlapping $d\pi(Ru) \rightarrow \pi^*(bpy)$ and $d\pi(Ru) \rightarrow \pi^*(H_3L)$ transitions. The lowered symmetry removes the degeneracy of the π^* levels, which results in the appearance of a non-symmetrical MLCT band. The MLCT absorption maximum of complexes $[RuH_3L^{1-3}]^{6+}$ is red-shifted by about 9 nm compared with that of $Ru(bpy)_3^{2+}$ [10] because tripodal ligands have larger extent of π delocalization.

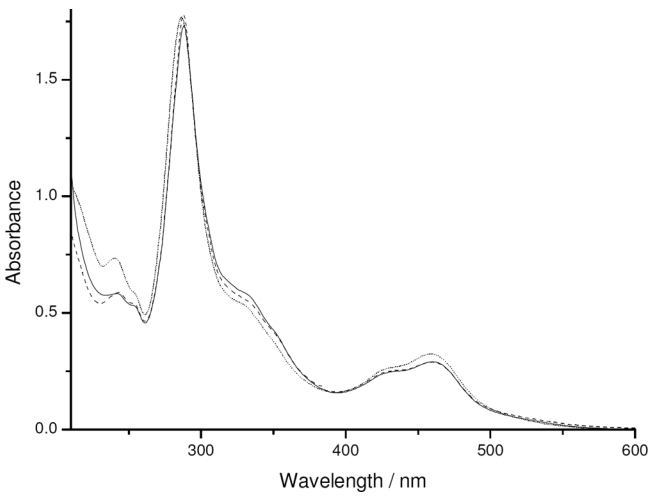

Figure 1. Absorption spectra of $[RuH_3L^1]^{6+}$ (short dot), $[RuH_3L^2]^{6+}$ (solid), and $[RuH_3L^3]^{6+}$ (dash) in CH_3CN solution at room temperature.

Emission band maxima and emission quantum yields of these Ru^{II} complexes are summarized in Table 1. Emission quantum yields are calculated relative to $Ru(bpy)_3^{2+}$ (Φ_{std} = 0.376) in 4:1 ethanol to methanol glassy matrix and $Ru(bpy)_3^{2+}$ (Φ_{std} = 0.062) in deoxygenated CH_3CN.[11] The equation $\Phi_{em} = (\eta_{compd}^2 / \eta_{std}^2)(A_{std} / A_{compd})(I_{compd} / I_{std})\Phi_{std}$ is used to calculate quantum yields. Upon excitation into the MLCT band of the complexes, $[RuH_3L^{1-3}]^{6+}$ show intense emissions at around 592 nm in CH_3CN solution at room temperature, and at around 584 nm in ethanol/methanol (4:1) glassy matrix at 77 K (Figure 2), which are characteristic of the triplet MLCT $d\pi(Ru) \rightarrow d\pi^*$ emission state.

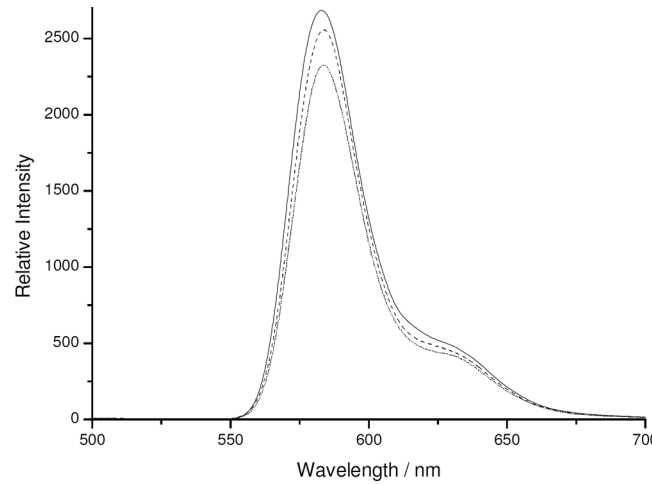

Figure 2. Emission spectra of $[RuH_3L^1]^{6+}$ (dash), $[RuH_3L^2]^{6+}$ (solid), and $[RuH_3L^3]^{6+}$ (short dot) in EtOH/MeOH (4:1) glassy matrix at 77 K.

pH Dependent Spectroscopic Properties

The pH dependence of the ground-state and excited-state properties of these complexes was investigated by UV/Vis absorption and fluorescence spectra, respectively. UV/Vis ab-

Table 1. Photophysical data of the Ru^{II} polypyridyl complexes $[RuH_3L^{1-3}]^{6+}$.

	Absorption [a]	Emission [b]			
Complex		298 K		77 K	
	λ_{max}, /nm ($10^4\varepsilon$, M^{-1}·cm^{-1})	λ_{max} /nm	Φ	λ_{max} /nm	Φ
$[RuH_3L^1]^{6+}$	459 (6.48)	592	0.077	584	0.442
	326 (10.94)				
	286 (35.38)				
	240 (14.71)				
$[RuH_3L^2]^{6+}$	460 (5.81)	592	0.083	583	0.463
	327 (11.91)				
	287 (33.60)				
	243 (11.66)				
$[RuH_3L^3]^{6+}$	459 (5.77)	592	0.073	584	0.392
	326 (11.41)				
	286 (35.57)				
	243 (11.76)				

a) 5×10^{-6} mol·L^{-1} in CH_3CN solution at room temperature. b) The uncertainty in quantum yield is 10 %.

sorption and fluorescence pH spectroscopic titrations of these complexes are carried out in acetonitrile-Briton–Robinson buffer (1:1) solution with NaCl (0.2 mol·L^{-1}) to keep a constant ionic strength. The pH titrations are carried out over the pH range 1.82–11.55 and the spectral changes with pH are reversible.

Figure 1 shows the UV/Vis absorption spectra of complex $[RuH_3L^1]^{6+}$ as a function of pH. Complex $[RuH_3L^1]^{6+}$ undergoes two successive deprotonation processes over the pH range 1.82–11.55. Upon increasing pH from 1.82 to 7.19 (Figure 3a), the absorption intensity of the MLCT band at 458 nm, the ligand H_3L^1-centered intraligand $\pi \rightarrow \pi^*$ transition band at 318 nm, and the bipyridine-centered intraligand $\pi \rightarrow \pi^*$ transition band at 285 nm are unchanged. The band at 238 nm is red-shifted to 240 nm accompanied by a slight decrease in the intensity. One isosbestic point at 215 nm appears during the process. Several methods can be used to determine the pK_a values.[12] The spectrophotometric method already described in the literature for other ruthenium complexes is chosen.[13] Plots of absorbance at 230 nm versus pH for complex $[RuH_3L^1]^{6+}$ is in the inset of Figure 3a. The figure has the expected sigmoidal shape, with the pH at the point of inflection giving the first ground-state ionization constant pK_{a1} value of 4.63. Spectral changes are attributed to the concurrent dissociation of three protons on protonated imidazole rings. Further increasing pH from 7.19 to 11.55 can induce the deprotonation on neutral imidazole rings (Figure 3b). Bands at 458 and 285 nm are red-shifted to 463 and 288 nm, respectively, accompanied by a slight decrease in the intensity; the band at 318 nm is red-shifted to 328 nm with an obvious increase in the intensity, the intensity of the low point at 490 nm is increased. The occurrence of three isosbestic points at 250, 403, and 463 nm indicate the presence of two species in equilibrium. The value of the second ground-state ionization constant pK_{a2} is 9.45. Two ground-state ionization constants pK_{a1} and pK_{a2} are compared with those of the analogous Ru^{II} complexes. The first ionization constant of the protonated imidazole ring on the complex is similar to the corresponding pK_{a1} value of 4.16 for $[(bpy)_2Ru(ebpibcH_2)Ru(bpy)_2]^{4+}$ [5c] and 4.11 for $[(bpy)_2Ru(bpibH_2)Ru(bpy)_2]^{4+}$.[5d] The ionization constant of the neutral imidazole rings on the complex is similar to the corresponding value of 9.65 for $[(bpy)_2Ru(ebpibcH_2)Ru(bpy)_2]^{4+}$ and 9.75 for $[(bpy)_2Ru(bpibH_2)Ru(bpy)_2]^{4+}$.

Fluorescence spectra changes of complex $[RuH_3L^1]^{6+}$ as a function of pH are shown in Figure 4. Emission intensity increases by about 20 % and the emission maxima are blue-shifted from 595 to 591 nm by increasing pH from 1.82 to 7.19 (Figure 4a). $[RuH_3L^1]^{6+}$ acts as an off-on fluorescence pH switch during the process. Fluorescence of complex $[RuH_3L^1]^{6+}$ is quenched at lower pH when the imidazole rings are protonated, because the ligand containing protonated imidazole rings is a better electron acceptor than bipyridine, the value of ΔE between the ligand π^* orbital and metal π orbital becomes large if bipyridine is replaced by imidazole-containing ligand.[14] Consequently, population of the MLCT excited state is more efficient for $[RuH_3L^1]^{6+}$ and $[RuH_3L^1]^{6+}$ is essentially strong emissive at room temperature. Further increasing pH from 7.19 to 11.55 (Figure 4b), the emission intensity decreases steadily to less than 24 % of the original emission intensity, and the emission maximum is obviously red-shifted from 591 to 604 nm. This on-off ratio is moderate compared with the reported data of imidazole-containing mononuclear and dinuclear Ru^{II} complexes congeners.[5] However, trinuclear imidazole-containing Ru^{II} complexes with such large luminescence on-off ratio over a narrow pH region have not yet been reported. Complex $[RuH_3L^1]^{6+}$ acts as an effective on-off fluorescence pH switch over the pH range. This behavior may involve rapid radiationless decay.[15] It has been well documented that the energy of the metal-centered excited state depends on the ligand field strength, which in turn depends on the σ-donor and π-acceptor properties of the ligand. The negative charge on the deprotonated imidazole rings can be delocalized over the whole π framework, which decreases the σ-donor and increases the π-acceptor capacity of the tripodal ligand, resulting in weakening of the ligand field strength around the metal atom and in turn lowering the metal σ* orbitals.[16] The

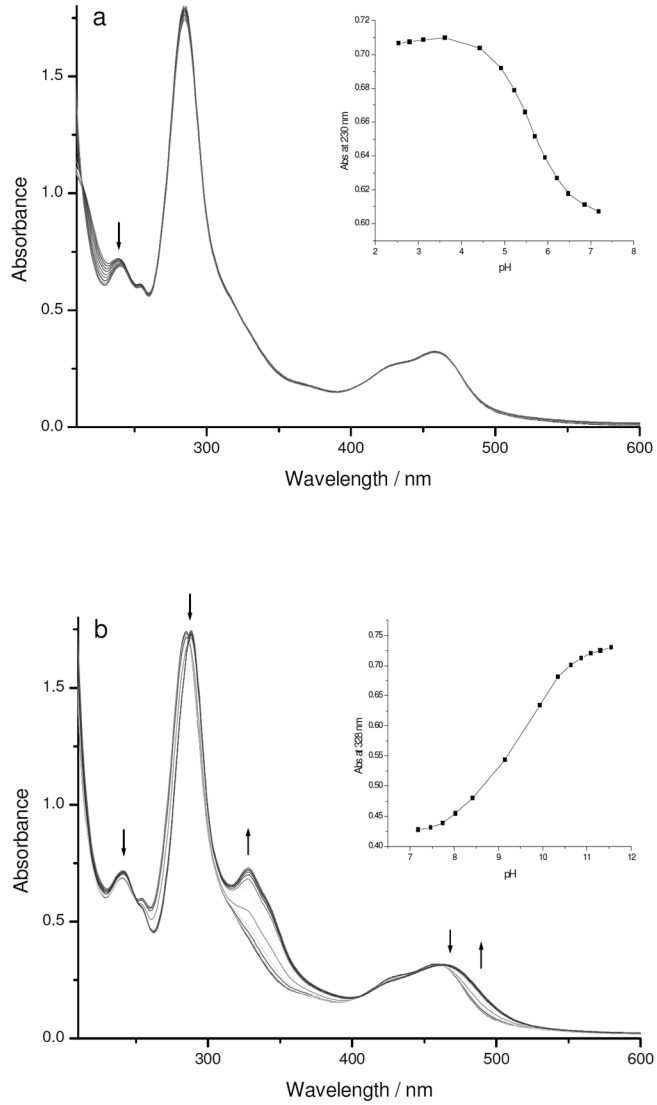

Figure 3. Absorption spectra changes of complex $[RuH_3L^1]^{6+}$ upon increasing the pH: (a) from 1.82 to 7.19; (b) from 7.19 to 11.55.

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value of ΔE between the metal σ* orbital and metal π orbital of the deprotonated complex $[RuL^1]^{3+}$ is lower than that of complex $[RuH_3L^1]^{6+}$.

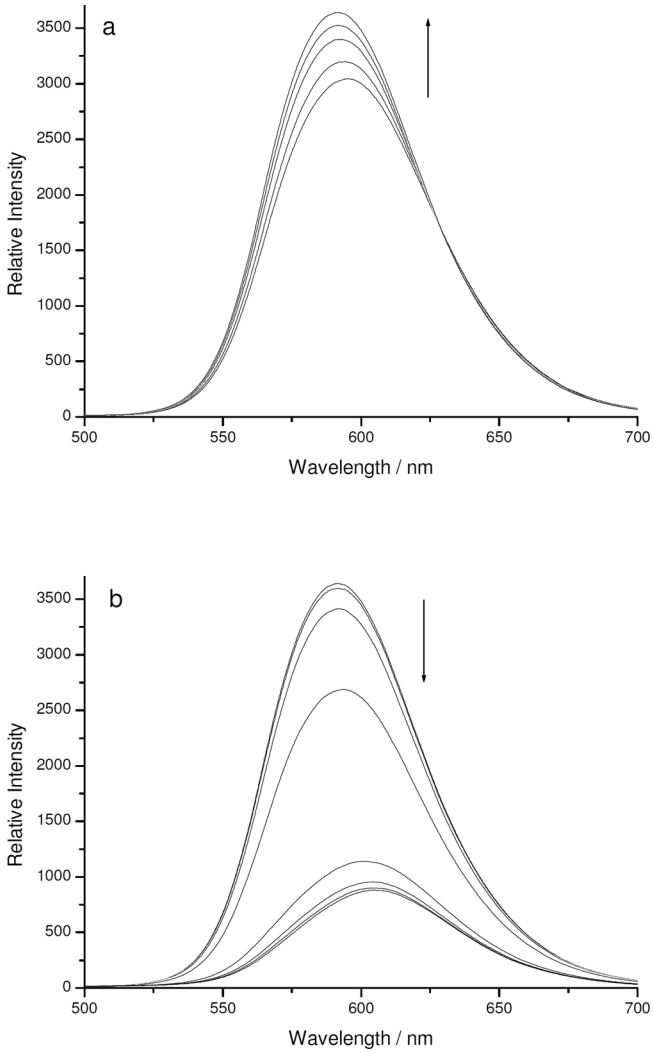

Figure 4. Emission spectra changes of complex $[RuH_3L^1]^{6+}$ upon increasing the pH: (a) from 1.82 to 7.19; (b) from 7.19 to 11.55.

Consequently, population of the metal charge excited state is very efficient for deprotonated complex and this complex is essentially weakly emissive at room temperature. Excited-state ionization constants, pK_a^*, could be roughly evaluated on the basis of the Förster cycle, [14] which correlates pK_a^* with pK_a thermodynamically by equation $pK_a^* = pK_a + (0.625 / T)(\nu_B - \nu_{HB})$, in which ν_B and ν_{HB} are pure 0–0 transitions in cm^{-1} for the basic and acidic species, respectively. In practice, ν_B and ν_{HB} are often difficult or even impossible to obtain. A good approximation is to use the emission maxima for ν_B and ν_{HB} because protonation equilibrium is almost certainly established between the ^{3}MLCT states.[17] Therefore, the energies of the emission maxima in wavenumbers are used in equation, and two excited-state ionization constants of $pK_{a1}^* = 4.53$, and $pK_{a2}^* = 9.78$ are thus obtained. The value of pK_{a1}^* is simlar to the value of pK_{a1}, whereas the value of pK_{a2}^* is 0.38 pK_a unit greater than pK_{a2}^*, indicating that the electron density of excited state is higher than the ground state and the excited electron is directed on ligand H_3L^1 rather than bipyridine. The increase in electron density on the ligand H_3L^1 increases its basicity and, therefore, increases the excited state pK_a^* value.

The spectroscopic properties of complexes $[RuH_3L^2]^{6+}$ and $[RuH_3L^3]^{6+}$ are similar to those of complex $[RuH_3L^1]^{6+}$. $[RuH_3L^2]^{6+}$, and $[RuH_3L^3]^{6+}$ also undergo two successive deprotonation processes over the pH range 1.82 to 11.55 with a maximum on-off ratio of 5, two ground-state ionization constants are $pK_{a1} = 4.52$, 4.36 and $pK_{a2} = 9.36$, 9.23, the values of two excited state ionization constants pK_{a1}^*, and pK_{a2}^* are 4.47, 4.28, and 9.68, 9.61, respectively.

Conclusions

Three trinuclear Ru^{II} polypyridyl complexes with imidazole fragments uncoordinated to the metal ions were synthesized. The absorption and emission spectra of complexes are strongly dependent on the solution pH. They behave as "off-on-off" fluorescence pH switch through two different mechanisms. Especially over the pH range from 7.74 to 10.64, complexes $[RuH_3L^{1-3}]^{6+}$ experience obvious variations in the UV/Vis absorption and fluorescence spectra with a maximum on-off ratio of 5. These complexes are interesting candidates for pH variation measurement due to their pH-dependent spectroscopic properties.

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References

[1] a) K. Sénéchal-David, S. J. A. Pope, S. Quinn, S. Faulkner, T. Gunnlaugsson, *Inorg. Chem.* **2006**, *45*, 10040; b) T. L. Easun, W. Z. Alsindi, N. Deppermann, M. Towrie, K. L. Ronayne, X. Z. Sun, M. D. Ward, M. W. George, *Inorg. Chem.* **2009**, *48*, 8759; c) G. Chen, J.-L. Xia, Z.-Y. Li, G.-A. Yu, S. Jin, S.-H. Liu, *J. Organomet. Chem.* **2010**, *695*, 323; d) M. Cavazzini, S. Quici, C. Scalera, F. Puntoriero, G. La Ganga, S. Campagna, *Inorg. Chem.* **2009**, *48*, 8578; e) Y. Sun, S. N. Collins, L. E. Joyce, C. Turro, *Inorg. Chem.* **2010**, *49*, 4257; f) B. Ventura, A. Barbier, F. Barigelletti, J. B. Seneclauze, P. Retailleau, R. Ziessel, *Inorg. Chem.* **2008**, *47*, 7048; g) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *73*, 759; h) T. Saita, H. Nitadori, A. Inagaki, M. Akita, *J. Organomet. Chem.* **2009**, *694*, 3125; i) R. T. F. Jukes, B. Bozic, P. Belser, L. De Cola, F. Hartl, *Inorg. Chem.* **2009**, *48*, 1711; j) M. W. Cooke, G. S. Hanan, F. Loiseau, S. Campagna, M. Watanabe, Y. Tanaka, *J. Am. Chem. Soc.* **2007**, *129*, 10479; k) T. L. Easun, W. Z. Alsindi, M. Towrie, K. L. Ronayne, X.-Z. Sun, M. D. Ward, M. W. George, *Inorg. Chem.* **2008**, *47*, 5071; l) C.-F. Wang, J.-L. Zuo, J.-W. Ying, T. Ren, X.-Z. You, *Inorg. Chem.* **2008**, *47*, 9716.

[2] a) T. Gunnlaugsson, J. P. Leonard, K. Sénéchal, A. J. Harte, *J. Am. Chem. Soc.* **2003**, *125*, 12062; b) P. Pallavicini, V. Amendola, C. Massera, E. Mundum, A. Taglietti, *Chem. Commun.* **2002**, 2452; c) Y. D. Fernandez, F. Foti, C. Mangano, P. Pallavicini, S. Patroni, A. P. Gramatges, S. R. Calvo, *Chem. Eur. J.* **2006**, *12*, 921; d) M. Licini, J. A. G. Williams, *Chem. Commun.* **1999**,

1943; e) C. P. McCoy, F. Stomeo, S. E. Plush, T. Gunnlaugsson, *Chem. Mater.* **2006**, *18*, 4336; f) K. Sénéchal-David, J. P. Leonard, S. E. Plush, T. Gunnlaugsson, *Org. Lett.* **2006**, *8*, 2727.

[3] a) T. Lazarides, T. L. Easun, C. V. Marti, W. Z. Alsindi, M. W. George, N. Deppermann, C. A. Hunter, H. Adams, W. D. Ward, *J. Am. Chem. Soc.* **2007**, *129*, 4014; b) B. Sun, J. X. Guan, L. Xu, B. L. Yu, L. Jiang, J. F. Kou, L. Wang, X. D. Ding, H. Chao, L. N. Ji, *Inorg. Chem.* **2009**, *48*, 4637; c) A. A. Marti, C. A. Puckett, J. Dyer, N. Stevens, S. Jockusch, J. Ju, J. K. Barton, N. J. Turro, *J. Am. Chem. Soc.* **2007**, *129*, 8680; d) Y. Cui, H. J. Mo, J. C. Chen, Y. L. Niu, Y. R. Zhong, K. C. Zheng, B. H. Ye, *Inorg. Chem.* **2007**, *46*, 6427; e) D. A. Jose, P. Kar, D. Koley, B. Ganguly, W. Thiel, H. N. Ghosh, A. Das, *Inorg. Chem.* **2007**, *46*, 5576; f) C. Kaes, A. Katz, M. W. Hosseini, *Chem. Rev.* **2000**, *77*, 3553; g) H. D. Batey, A. C. Whitwood, A.-K. Duhme-Klair, *Inorg. Chem.* **2007**, *46*, 6516; h) L. Herman, B. Elias, F. Pierard, C. Moucheron, A. K. Mesmaeker, *J. Phys. Chem. A* **2007**, *111*, 9756; i) P. D. Beer, F. Szemes, P. Passaniti, M. Maestri, *Inorg. Chem.* **2004**, *43*, 3965; j) T. Lazarides, T. A. Miller, J. C. Jeffery, T. K. Ronson, H. Adams, M. D. Ward, *Dalton Trans.* **2005**, 528.

[4] a) T. Ayers, N. Caylor, G. Ayers, C. Godwin, D. J. Hathcock, V. Stuman, S. J. Slattery, *Inorg. Chim. Acta* **2002**, *328*, 33; b) M. Haga, T. Takasugi, A. Tomie, M. Ishizuya, T. Yamada, *Dalton Trans.* **2003**, 2069; c) S. Baitalik, U. Flörke, K. Nag, *J. Chem. Soc., Dalton Trans.* **1999**, 719; d) M. Haga, M. M. Ali, S. Koseki, K. Fujimoto, A. Yoshimura, K. Nozaki, T. Ohno, K. Nakajima, D. J. Stufkens, *Inorg. Chem.* **1996**, *35*, 3335; e) T. Ohno, K. Nozaki, M. Haga, *Inorg. Chem.* **1992**, *31*, 548; f) M. Haga, T. Ano, K. Kano, S. Yamabe, *Inorg. Chem.* **1991**, *30*, 3843; g) K.-Z. Wang, L.-H. Cao, G.-Y. Bai, L.-P. Jin, *Inorg. Chem. Commun.* **2002**, *5*, 841.

[5] a) S. H. Fan, K. Z. Wang, W. C. Yang, *Eur. J. Inorg. Chem.* **2009**, 508; b) A. Quaranta, F. Lachaud, C. Herrero, R. Guillot, M. F. Charlot, W. Leibl, A. Aukauloo, *Chem. Eur. J.* **2007**, *13*, 8201; c) F. Liu, K. Z. Wang, G. Bai, Y. Zhang, L. Gao, *Inorg. Chem.* **2004**, *43*, 1799; d) H. Chao, B. H. Ye, H. Li, R. H. Li, J. Y. Zhou, L. N. Ji, *Polyhedron* **2000**, *19*, 1975; e) F. Gao, H. Chao, F. Zhou, B. Peng, L.-N. Ji, *Inorg. Chem. Commun.* **2007**, *10*, 170; f) Y. Z. Ma, H. J. Yin, K. Z. Wang, *J. Phys. Chem. B* **2009**, *113*, 11039; g) H. Chao, B.-H. Ye, Q.-L. Zhang, L.-N. Ji, *Inorg. Chem. Commun.* **1999**, *2*, 338; h) B.-W. Jing, T. Wu, C.-H. Tai, M.-H. Zhang, T. Shen, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 71749; i) A. Quaranta, F. Lachaud, C. Herrero, R. Guillot, M. F. Charlot, W. Leibl, A. Aukauloo, *Chem. Eur. J.* **2007**, *13*, 8201; j) Y. Xiong, X.-F. He, X.-H. Zou, J.-Z. Wu, X.-M. Chen, L.-N. Ji, R.-H. Li, J.-Y. Zhou, K.-B. Yu, *J. Chem. Soc., Dalton Trans.* **1999**, 19.

[6] J. Závada, M. Pánková, P. Holý, M. Tichý, *Synthesis* **1994**, *110*, 1132.

[7] C. Hiort, P. Lincoln, B. Norden, *J. Am. Chem. Soc.* **1993**, *115*, 3448.

[8] B. P. Sullivan, D. J. Salmon, T. J. Meyer, *Inorg. Chem.* **1978**, *17*, 3334.

[9] B. E. A. Steck, A. R. Day, *J. Am. Chem. Soc.* **1943**, *65*, 452.

[10] D. P. Rillema, K. B. Mack, *Inorg. Chem.* **1982**, *21*, 3849.

[11] a) R. J. Watts, G. A. Crosby, *J. Am. Chem. Soc.* **1972**, *94*, 2606; b) E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar, T. J. Meyer, *Inorg. Chem.* **1985**, *24*, 2755; c) E. Amouyal, A. Homsi, J. C. Chambron, J. P. Sauvage, *J. Chem. Soc., Dalton Trans.* **1990**, 1841.

[12] a) Z. J. Jia, T. Ramstad, M. Zhong, *Electrophoresis* **2001**, *22*, 1112; b) N. R. De Tacconi, R. O. Lezna, R. Konduri, F. Ongeri, K. Rajeshwar, F. M. MacDonnell, *Chem. Eur. J.* **2005**, *11*, 4327; c) T. N. Brown, N. Mora-Diez, *J. Phys. Chem. B* **2006**, *110*, 20546; d) B. Knobloch, H. Sigel, A. Okruszek, R. K. O. Sigel, *Org. Biomol. Chem.* **2006**, *4*, 1085.

[13] a) A. Rugge, C. D. Clark, M. Z. Hoffman, D. P. Rillema, *Inorg. Chim. Acta* **1998**, *279*, 200; b) K. O'Donoghue, J. C. Penedo, J. M. Kelly, P. E. Kruger, *Dalton Trans.* **2005**, 1123.

[14] R. Grigg, W. D. J. A. Norbert, *J. Chem. Soc., Chem. Commun.* **1992**, 1300.

[15] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85.

[16] a) R. H. Fabian, D. M. Klassen, R. W. Sonntag, *Inorg. Chem.* **1980**, *19*, 1977; b) J. M. Kelly, C. Long, C. M. O'Connell, J. M. Vos, H. A. Tinnemans, *Inorg. Chem.* **1983**, *22*, 2818.

[17] G. Y. Zheng, Y. Wang, D. P. Rillema, *Inorg. Chem.* **1996**, *35*, 7118.

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