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First Synthesis of Porphyrin-Fused 1,10-Phenanthroline−Ruthenium(II) Complexes

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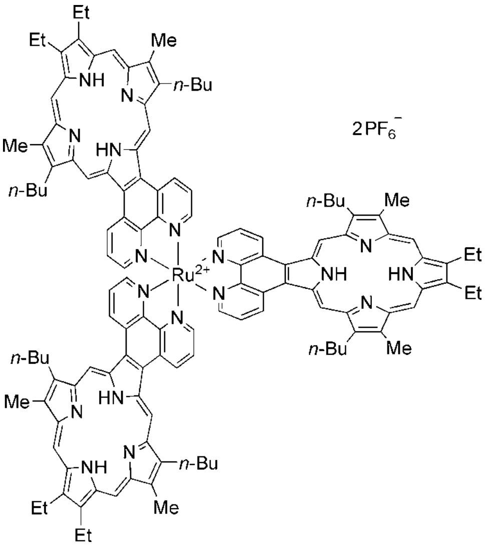
ABSTRACT



Synthesis of [Ru(phenP)$_3$](PF$_6$)$_2$, where phenP = phenanthrolinoporphyrin, has been achieved by the reaction of phenanthrolinoporphyrins with RuCl$_3$ for the first time. The phenP reacted with Ru(II) to form RuL$_2$(phenP)$^{2+}$ complexes (L = 2,2′-bipyridine or 1,10-phenanthroline), which were converted into the dyads Ru−phenP(Zn) on treatment with zinc acetate.

1,10-Phenanthroline has been extensively used as an important ligand of metal complexes such as ruthenium or lanthanide in coordination chemistry because of their unique and interesting photophysical and photochemical properties.[1,2] The chemistry of ruthenium(II) complexes containing 1,10-phenanthrolines, which were more rigid and symmetrical ligands compared to 2,2′-bipyridine, have especially developed as photosensitizers for dye-sensitized solar cells. On the other hand, Ru(II) complexes containing phenanthroline-based ligands fused with π-conjugated molecules have also attracted the interest of many chemists.[3,4] Recently, Guldi et al. have reported the synthesis of the phthalocyanine-fused pyrazino[2,3-*f*]phenanthroline complexes and their photoinduced energy-transfer processes.[5] Although phenanthrolinoporphyrins have been synthesized by Lash et al.[6] and Ru(II) complexes containing pyrrole-fused phenanthroline have been reported by Rillema et al.,[4] the complexes of

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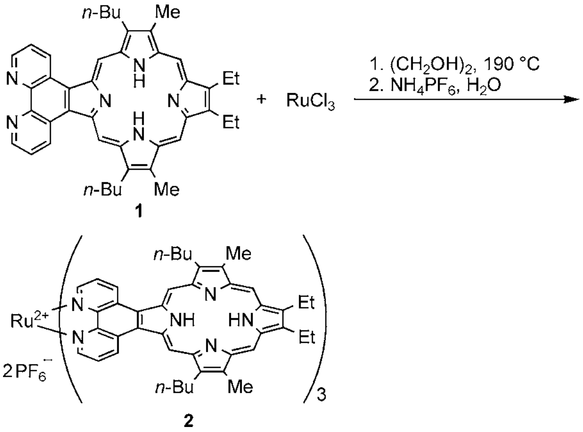
Ru(II)−phenanthroline fused with porphyrins, analogues of phthalocyanines, have never been reported. On the other hand, Ru(II)−bipyridine complexes, covalently linked to porphyrins, have been well-known.[7] However, the synthesis of the Ru(II) complexes containing porphyrin directly conjugated with coordination sites such as phenanthroline at β-positions have never been achieved because of difficulty with their synthesis. Porphyrin-fused phenanthroline−Ru(II) complexes are attractive as highly conjugated chromophores on the basis of the porphyrin and Ru(II) complex. We report herein the first synthesis of Ru(II) complexes coordinated with phenanthroline fused with porphyrin.

Scheme 1. Preparation of [Ru(phenP)$_3$](PF$_6$)$_2$ (**2**)·2PF$_6^-$



The synthesis of [Ru(phenP)$_3$](PF$_6$)$_2$, where phenP = phenanthrolinoporphyrin (**1**), is shown in Scheme 1. Phenanthrolinopyrrole was prepared by the Barton−Zard reaction of 5-nitro-1,10-phenanthroline according to the literature procedure.[8,9] The [3 + 1] porphyrin synthesis by a tripyrrane containing phenanthrolinopyrrole, which was obtained by the condensation of α-unsubstituted phenanthrolinopyrrole with α-acetoxymethylpyrrole as a stable yellow powder, gave **1** in an excellent yield.[6] The ligand, phenP (**1**), reacted with Ru(III) chloride in ethylene glycol at 190 °C followed by the treatment with NH$_4$PF$_6$ to give **2**·2PF$_6^-$ as purple crystals in a 83% yield. MALDI-TOF mass spectrum of **2**·2PF$_6^-$ showed peaks at *m/z* 2222 and 1418, which were assigned to be [M − PF$_6$]$^+$ and [M − phenP − PF$_6$]$^+$ (Figure S10, Supporting Information). The product is stable and fully characterized by physical and spectral methods including elemental analysis as shown in the Supporting Information.

On the other hand, [Ru(bpy)$_2$(phenP)](PF$_6$)$_2$ (**3a**)·2PF$_6^-$ and [Ru(phen)$_2$(phenP)](PF$_6$)$_2$ (**4a**)·2PF$_6^-$, where bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline, were prepared by reacting **1** directly with *cis*-Ru(bpy)$_2$Cl$_2$[10] and *cis*-Ru(phen)$_2$Cl$_2$[11] in DMF at 150 °C, followed by an exchange of the counteranion with PF$_6^-$ by the addition of KPF$_6$ in 97% and 89% yields, respectively (Figure 1). These complexes showed peaks corresponding to [M − PF$_6$]$^+$, [M − 2PF$_6$]$^+$, and [M − bpy(or phen) − 2PF$_6$]$^+$ in the MALDI-TOF MS as shown in Figures S11 and S13 (Supporting Information). Ru complexes coordinated with free base phenP **3a**·2PF$_6^-$ and **4a**·2PF$_6^-$ were treated with zinc acetate to give the Ru−Zn binuclear metal complexes **3b**·2PF$_6^-$ and **4b**·2PF$_6^-$ in 14% and 82% yields, respectively.

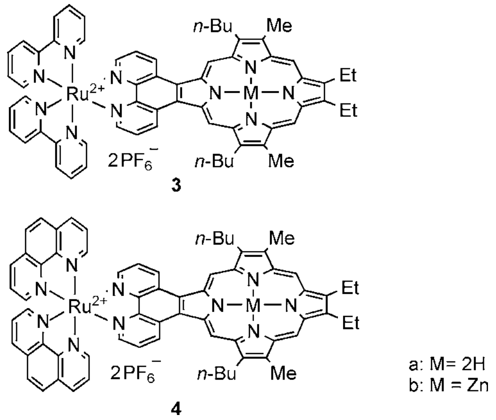


Figure 1. Molecular structures of **3**·2PF$_6^-$ and **4**·2PF$_6^-$.

The similar strategy and the subsequent retro-Diels−Alder reaction afforded the Ru(II) complexes containing π-expanded phenanthrolinoporphyrin as shown in Scheme 2. The condensation of α-unsubstituted phenanthrolinopyrrole with α-acetoxymethylpyrrole fused with bicyclo[2.2.2]octadiene (BCOD)[12] in refluxing acetic acid/ethanol gave tripyrrane **5** in a 91% yield as a stable pale orange powder. Tripyrrane **5** was treated with TFA, diluted with CHCl$_3$, and condensed with **6**. After neutralization with Et$_3$N and oxidation with DDQ, BCOD-fused phenanthrolinoporphyrin (phenCP, **7**) was obtained in a 53% yield.

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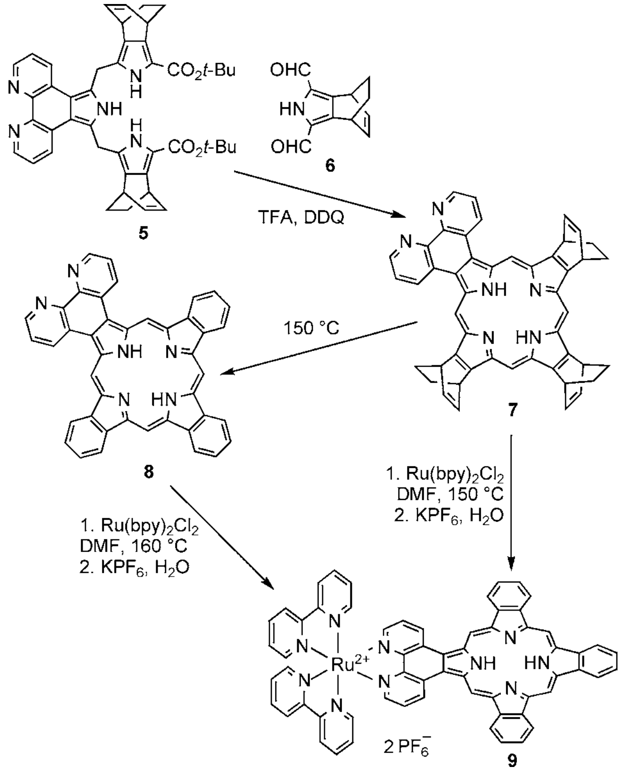
Scheme 2



A thermogravimetric analysis (TGA) curve of **7** is shown in Figure 2. The weight loss started at around 150 °C and ceased after 200 °C. The loss of weight was ca. 12%, consistent with the calculated value corresponding to three ethylene molecules. The retro-Diels−Alder reaction of phenCP (**7**) was carried out at 150 °C in vacuo in a glass tube oven as a solid to give phenanthrolinotribenzoporphyrin (phenBP, **8**) in a nearly quantitative yield.

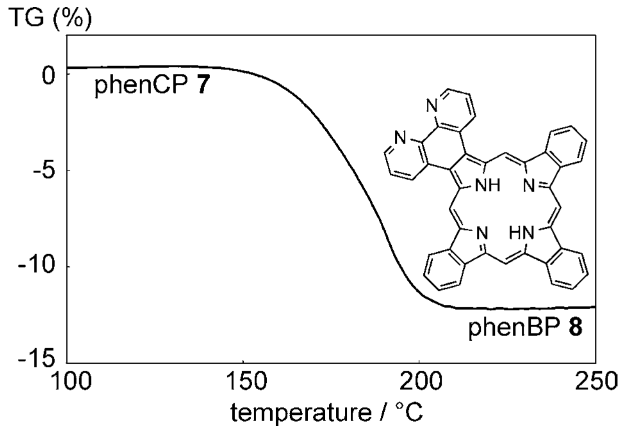


Figure 2. TGA of phenCP (**7**).

The reaction of phenCP (**7**) with *cis*-Ru(bpy)$_2$Cl$_2$[10] in refluxing DMF, followed by a treatment of KPF$_6$, resulted in a formation of [Ru(bpy)$_2$(phenBP)](PF$_6$)$_2$ (**9**)·2PF$_6^-$ via complexation and simulutaneous retro-Diels−Alder reaction of **7**. This reaction was carried out at 110−120 °C to give a mixture of Ru(II) complexes containing phenCP and phenanthrolinodibenzoporphyrin. PhenBP (**8**) was slightly dissolved in DMF at room temperature and reacted with *cis*-Ru(bpy)$_2$Cl$_2$ in refluxing DMF to give **9**·2PF$_6^-$ in 73% yield.

The UV−vis absorption and fluorescence emission spectra of Ru(II) complexes containing **1** are shown in Figure 3.

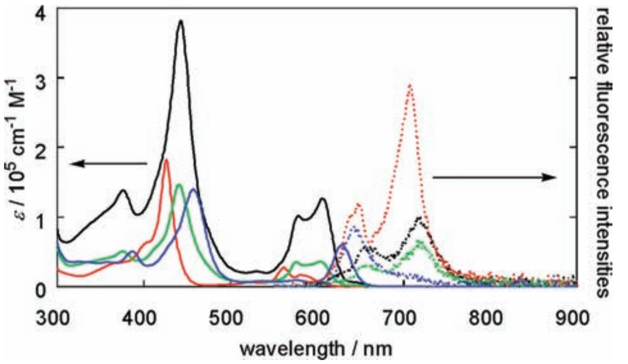


Figure 3. UV−vis absorption (solid lines) and fluorescence emission (dotted lines) spectra of **1** (red lines), **2**·2PF$_6^-$ (black lines), **3a**·2PF$_6^-$ (green lines), and **3b**·2PF$_6^-$ (blue lines) in PhCN. Fluorescence spectra were measured at 3.2×10^{-7} M.

The Soret bands of Ru−phenP complexes **2**·2PF$_6^-$ and **3a**·2PF$_6^-$ appeared at 442 nm (log ε 5.58) and 440 (5.17), respectively. The absorbance of tris(phenP)Ru^{2+} complex **2**·2PF$_6^-$ is stronger than that of **3**·2PF$_6^-$. Ru-phenP(Zn) complex **3b**·2PF$_6^-$ showed the Soret band at 457 nm and the Q-band at 629 nm. While covalently linked porphyrin−bipyridine−Ru(II) complexes showed a red shift of the Q-band and the broadening of the Soret and Q bands,[7] π-conjugated porphyrin−phenanthroline−Ru(II) complexes **2** and **3** showed a red shift of both the Soret and Q bands by 15−25 nm compared to those of phenP (**1**). The absorption and emission spectra of [Ru(bpy)$_2$(phenP)](PF$_6$)$_2$ **3**·2PF$_6^-$ (Figure 3) are very similar to those of [Ru(phen)$_2$-(phenP)](PF$_6$)$_2$ **4**·2PF$_6^-$ (Figures S5 and S6, Supporting Information). No influence derived from the difference of the ligands such as bpy or phen is observed. The fluorescence emission spectra with excitation at their Soret bands showed two bands at 640−650 and 710−720 nm for free base phenP **1** and complexes **2**·2PF$_6^-$ and **3a**·2PF$_6^-$, while that of phnP(Zn) complex **3b**·2PF$_6^-$ showed a single band at 640 nm. The fluorescence intensity of Ru−phenP complexes **2**−**4**·2PF$_6^-$ are weaker than that of phenP (**1**).

The absorption and emission data, the fluorescence lifetimes (τ_f), and the absolute quantum yields (Φ_f) are summarized in Table 1. The fluorescence intensity of **1** was stronger than those of Ru−**1** complexes as shown in Figure 3. This observation was consistent with their absolute quantum yields (8−9% for **1** and 2−4% for **2**−**4**·2PF$_6^-$). Similar results were obtained for phenBP (**8**)

Table 1. Absorbance, Fluorescence, Absolute Quantum Yields (Φ_f), and Fluorescence Lifetimes (τ_f) of phenPs and Ru−phenP Complexes

compd	λ_{abs}/nm (log ϵ)	λ_{em}/nm	Φ_f (%) (λ_{ex}/nm)	τ_f/ns
1	366 (4.53)	639	9 (401)	12.2
	404 (4.81)	707	8 (425)	
	426 (5.26)			
	524 (3.84)			
	561 (4.45)			
	581 (4.23)			
2·2PF$_6^-$	376 (5.15)	648	3 (377)	3.0 (92%)
	442 (5.58)	707	4 (426)	8.6 (8%)
	578 (5.01)		2 (443)	
	606 (5.11)			
3a·2PF$_6^-$	376 (4.71)	656	4 (377)	3.6
	440 (5.17)	719	3 (440)	
	576 (4.55)			
	603 (4.56)			
3b·2PF$_6^-$	387 (4.71)	646	3 (385)	0.6
	457 (5.15)		2 (455)	
	537 (3.92)			
	576 (3.97)			
	629 (4.78)			
4a·2PF$_6^-$	377 (4.70)	656	3 (377)	4.0
	440 (5.15)	719	2 (440)	
	531 (3.89)			
	576 (4.54)			
	603 (4.54)			
4b·2PF$_6^-$	387 (4.74)	644	3 (385)	0.7
	457 (5.15)		3 (455)	
	536 (3.93)			
	576 (3.98)			
	628 (4.78)			
7	365 (4.59)	642	8 (362)	12.0
	409 (4.99)	706	7 (401)	
	425 (5.32)		6 (425)	
	488 (3.71)		17 (514)	
	519 (4.03)			
	552 (4.53)			
	579 (4.11)			
8	416 (4.88)	684	35 (361)	7.7
	440 (5.46)	719	33 (416)	
	550 (4.12)	742	34 (440)	
	585 (4.69)		46 (550)	
	631 (4.04)			
	681 (4.80)			
9·2PF$_6^-$	409 (4.73)	701	11 (414)	3.4
	452 (5.17)	758	13 (454)	
	549 (4.22)		26 (549)	
	581 (4.45)			
	663 (4.44)			
	694 (4.79)			

and its Ru complex **9**·2PF$_6^-$. The fluorescence lifetimes of phenPs (**1**), phenCP (**7**), and phenBP (**8**) were determined to be 12.2, 12.0, and 7.7 ns, respectively, while those of the Ru complexes were 3−4 ns for **2**, **3a**, **4a**, and **9**·2PF$_6^-$ (free-base porphyrin ligands) and <1 ns for **3b** and **4b**·2PF$_6^-$ (Zn−porphyrin ligand). Thus, the fluorescence of Ru−phenP complexes was quenched compared to that of phenPs. The lifetimes of Ru(II)−phenP complexes **2**−**4** and **9**·2PF$_6^-$ were much shorter than those of the Ru(II) complexes with similar aromatic ring ligands.[3−5] No excitation wavelength dependence in the fluorescence spectra was observed as shown in Figure S9 (Supporting Information). These facts indicate that the observed emission peaks were not the MLCT state emission. Absorption bands assigned to the ^{1}MLCT transition of the similar Ru(II) chromophores are generally observed at around 450 nm.[3−5] The strong bands seen around 450 nm in the absorption spectra of **2**−**4** and **9**·2PF$_6^-$ would be only the Soret bands of the phenP moiety. Therefore, the fluorescence of Ru(II)-phenP complexes **2**−**4** and **9**·2PF$_6^-$ were emitted from Q bands of the phenP moiety.

In summary, we have succeeded in preparing a series of ruthenium(II) complexes coordinated with 1,10-phenanthroline fused with porphyrins at β-positions for the first time. The selective metalation of the cavity and the periphery of phenP **1** afforded the Ru−Zn binuclear metal complexes **3b**·2PF$_6^-$ and **4b**·2PF$_6^-$. Their absorption and emission intensities depended on the number of the coordinating phenP. Their fluorescence, which was emitted from the Q-band of the phenP moiety, was partially quenched compared to those of phenPs **1**, **7**, and **8**.

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Supporting Information Available: General and experimental details and copies of MALDI-TOF mass, ^{1}H NMR, absorption, and emission spectra of the reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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