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Redox Gradations in Ruthenium Porphycene Complexes and the Porphyrin Analogs: Axial and Macrocyclic Ligand Effects

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This paper reports synthesis and electrochemistry of six-coordinate ruthenium porphyrin isomers including six novel porphycene complexes with substituted pyridines in the axial positions, in which redox potential control of reversible Ru^{II}/Ru^{III} processes is successfully achieved over a 0.7-V potential region by varying the axial ligands and tetrapyrrole ligand structure and substituents.

Porphycene[1] is a structural isomer of porphyrin, in which the tetrapyrrole macrocycle framework is arranged in a rectangular shape. This structural feature results in remarkable optical and photophysical properties and is also effectively utilized as photosensitizers for singlet oxygen generation[2] and photodynamic therapy agents.[3]

The free-base porphycene undergoes multiple redox processes due to the tetrapyrrole framework. The potential tuning of porphycene-based processes is well established through substituent modifications.[4] For metalloporphycenes, however, redox chemistry of metal-based redox processes has been limited, mostly concerned with metalloporphycenes containing first-row transition-metal ions.[5,6] Herein we report the synthesis and electrochemistry of a new series of ruthenium porphycene complexes, in which substituents on the axial pyridines and those of the tetrapyrrole periphery are systematically varied for redox potential control (Chart 1). The bis(pyridine)-type complexes are well known for ruthenium porphyrins[7] but, to our knowledge, the porphycene analogues have not been reported to date. The only example is [Ru(TPrPc)(CO)(ethanol)] or [Ru(TPrPc)(CO)] (TPrPc = tetra(*n*-propyl)porphycenato dianion),[8] which does not present Ru-based redox processes in a normal potential region owing to considerable stabilization of Ru^{II} by the strong π-accepting ligand CO. We show that redox potentials of the reversible Ru^{II}/Ru^{III} couple in the bis(pyridine)-type complexes are tuned considerably (ca. 0.5 V) by varying substituents on the pyridine rings and moderately by substituents on the tetrapyrrole periphery and the tetrapyrrole macrocycle structures, which eventually leads to a Ru^{II}/Ru^{III} potential shift over 0.7 V. Our present findings in sequential potential control, which we term "redox gradations" in this paper, are fairly remarkable in that such ligand-design-based strategy is demonstrated for the first time by using a systematic series of metalloporphycenes containing a single kind of transition-metal ions.

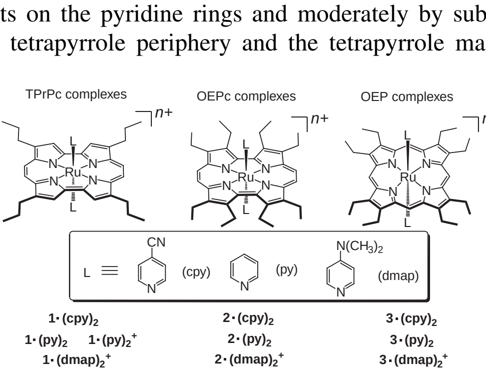
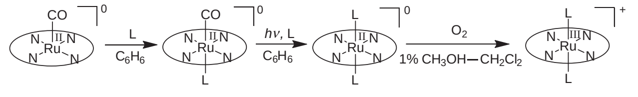


Chart 1. Ruthenium porphycenes and porphyrins examined in this study ($n = 0$ for Ru^{II} and $n = 1$ for Ru^{III}).

The free-base porphyrin isomers and the corresponding CO-coordinated complexes [Ru(por)(CO)] (por = TPrPc, OEPc, and OEP) were prepared according to the literature.[7,8] A series of six-coordinate complexes with *trans*-bis(pyridine derivatives) were prepared by reacting [Ru(por)(CO)] with a large excess amount of pyridine derivatives (L's) under UV-irradiation in deaerated C_6H_6.[9] The synthetic route is illustrated in Scheme 1. An intermediate [Ru(por)(CO)L] is formed instantaneously upon mixing [Ru(por)(CO)] and a large excess of L (the first step in Scheme 1; See also the Supporting Information for isolation of [Ru(TPrPc)(CO)(py)]). The bis(py) and bis(cpy) complexes were isolated in a neutral ($n = 0$) form involving Ru^{II} (the second step). For the bis(dmap) complexes, the initial photoproduct appeared to be Ru^{II} complexes but, during column chromatographic purification on alumina (1% CH_3OH–CH_2Cl_2) under aerobic conditions, they were eventually oxidized to form cationic ($n = 1$) complexes involving Ru^{III} (the third step). The more stable nature in a higher oxidation state for the bis(dmap) complexes arises from electron-donating ability of axial dmap ligands (see later).

A cationic bis(pyridine)–TPrPc complex $\mathbf{1}\cdot(py)_2^+$ was also obtained by performing the photoreaction in CH_2Cl_2 under aerobic conditions. EPR spectroscopy of a ClO_4^- salt of $\mathbf{1}\cdot(py)_2^+$ (77 K, frozen CH_2Cl_2) revealed g values of 2.35, 2.23, and 1.75, providing conclusive evidence for the presence of a Ru^{III} center ($S = 1/2$).[10] Further, a ^1H NMR spectrum of $\mathbf{1}\cdot(py)_2^+$ in $CDCl_3$ quite resembles that of a low-spin, iron(III) complex $[Fe(TPrPc)(py)_2]ClO_4$.[11]

The photochemical formation of the $[Ru(por)(L)_2]$ complexes was followed by UV–vis spectroscopy. The spectral change is presented in Figure 1 for the formation of $\mathbf{1}\cdot(py)_2$ as a typical example. Upon UV irradiation with a black light, the initial UV–vis spectrum of a C_6H_6 solution of [Ru(TPrPc)(CO)(py)] ($\lambda_{max} = 383$ and 611 nm) gradually changed, and a new species $[Ru(TPrPc)(py)_2]$ ($\mathbf{1}\cdot(py)_2$) was formed ($\lambda_{max} =$ 316, 340, 381, 447, 601, and 621 nm). Isosbestic points at 356, 417, 560, 564, 571, 577, 606, 617, and 628 nm were observed. An FTIR spectrum (KBr method) of [Ru(TPrPc)(CO)(py)]



Scheme 1. Formation of $[Ru(por)(L)_2]^{n+}$ complexes (por = TPrPc, OEPc, and OEP; L = cpy, py, and dmap.

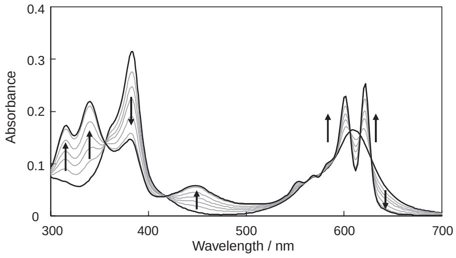


Figure 1. UV–vis spectra representing photoinduced CO dissociation from [Ru(TPrPc)(CO)(py)] (in C_6H_6 with external pyridine) to form [Ru(TPrPc)(py)$_2$] (**1**•(py)$_2$).

shows a strong CO stretch at 1935 cm^{-1} which completely disappeared after the photoreaction. An independent study by ^{1}H NMR spectroscopy (C_6D_6) supported the coordination of two pyridine molecules to one Ru^{II} center to form **1**•(py)$_2$.

As previously reported for [Ru(OEP)(CO)],[12] the photodissociation of CO occurs only when the complex was irradiated by UV light. In our ruthenium porphycenes, we also confirmed that the UV excitation (<430 nm, using band-pass filter) solely promoted the CO dissociation. The CO dissociation is well described by the first-order kinetics with a rate constant of $3.5(\pm0.1) \times 10^{-3}$ s^{-1} (298 K). Further details in photochemistry will be described in a separate paper.

Cyclic voltammetry was used to assess redox properties of ruthenium porphycenes and porphyrins. Figure 2 presents CVs of a total of nine complexes in 0.1 M n-Bu_4NClO_4–CH_2Cl_2 (M = mol dm^{-3}). In the potential region between +1.00 and −1.00 V vs. Ag/AgCl, all the complexes exhibit a reversible one-electron wave. For instance, redox couples appear at $E_{1/2} = -0.32$, −0.11, and +0.18 V for TPrPc complexes **1**•(dmap)$_2^+$, **1**•(py)$_2$, and **1**•(cpy)$_2$, respectively (solid lines in Figure 2). They are assigned to metal-centered Ru^{II}/Ru^{III} couples on the basis of established results for ruthenium porphyrin complexes. The observed redox potential shift, ranging in a 0.5-V region, is readily ascribed to electronic effects of the substituent on the pyridine ring; the more electron-withdrawing substituent pushes the potential to the positive direction. An analogous trend is seen for OEPc complexes **2**•(dmap)$_2^+$, **2**•(py)$_2$, and **2**•(cpy)$_2$ (broken lines) and OEP complexes **3**•(dmap)$_2^+$, **3**•(py)$_2$, and **3**•(cpy)$_2$ (dotted lines).

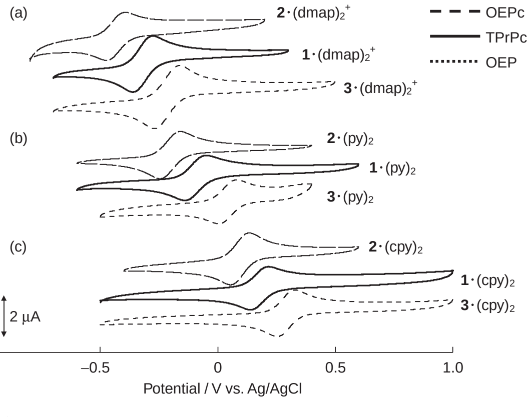


Figure 2. Redox behavior of nine ruthenium porphyrin isomers in 0.1 M n-Bu_4NClO_4–CH_2Cl_2. (a) Bis(dmap) complexes. (b) Bis(py) complexes. (c) Bis(cpy) complexes. Platinum (diameter, 3 mm), platinum wire, and Ag/AgCl electrodes were used as working, counter, and reference electrodes, respectively. [Complex] = 0.5 mM. Scan rate = 0.1 V s^{-1}.

Replacement of four n-Pr groups with eight Et groups on the porphycenato dianion (TPrPc → OEPc) resulted in a potential shift to a negative direction by ca. 0.1 V, while structural change in the macrocycle from porphycenenato dianion to porphyrinato dianion (OEPc → OEP) resulted in the positive shift by ca. 0.2 V. The notable extent of the macrocyclic ligand effects clearly demonstrates the presence of intramolecular $d\pi$(Ru)–$p\pi$(tetrapyrrole ligand) electronic interactions to a significant degree across the series. The three types of ligand effects thus provide the sequential redox shift over 0.7 V (Figure 2). It should be mentioned that porphycene- and porphyrin-based redox waves, which are detected in the more positive and negative potential region, were found to be quasi-reversible or irreversible, and the axial ligand influences were less significant.[9,13]

In summary, the synthetic strategy described here proves promising for controlling metal-based redox potentials of ruthenium porphyrin isomers in a desired direction and extent as much as 0.7 V. The present insight may find a considerable utility of ruthenium porphycenes, for instance, as new molecular components for potential-gradient materials.

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9 Experimental details and characterization data are provided in the Supporting Information which is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/.

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13 For comparison, a free-base H_2TPrPc shows reversible redox waves at $E_{1/2} = -1.25$, −0.88, and +1.02 V along with an irreversible wave at $E_{pa} = +1.55$ V under the identical conditions. The [Ru(TPrPc)(CO)(py)] complex shows TPrPc dianion-based waves at $E_{1/2} = -1.40$, −1.10, +0.81, and +1.25 V.

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