

Synthesis, Characterizations, and Intramolecular Quenching Behavior of an Axially-Linked Trinuclear Molecular Wire Containing Ruthenium(II) Porphycenes

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ABSTRACT: A new trinuclear complex $[\text{Ru}(\text{TPrPc}(\text{CO}))_2[\text{Ru}(\text{pytpy})_2](\text{PF}_6)_2$ (TPrPc = 2,7,12,17-tetra-*n*-propylporphycenato dianion and pytpy = 4'-(4-pyridyl)-2,2':6',2''-terpyridine) has been synthesized and characterized as the first example of a discrete molecular wire containing metalloporphycenes as a building block. The trinuclear complex shows multiple-step redox behavior in 0.1 M *n*-Bu₄NPF₆-dichloromethane. The mononuclear $[\text{Ru}(\text{pytpy})_2]^{2+}$ precursor shows emission at 640 nm (deaerated acetone, 298 K) upon illumination at the metal-to-ligand charge transfer (MLCT) band at 495 nm, but the trinuclear molecular wire is found to be non-emissive upon photoexcitation at the central $[\text{Ru}(\text{pytpy})_2]^{2+}$ entity, indicating an efficient quenching ability of the axially-linked, ruthenium(II)-porphycene chromophores in an intramolecular fashion.

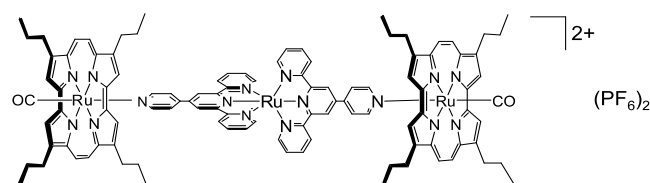
Porphycene is one of the constitutional isomers of porphyrin with a tetrapyrrolic N₄ cavity in a rectangular shape [1–4]. Chemistry of porphycene and metalloporphycene complexes [5,6] has been of considerable interest due to their intense absorption in the visible region [7], utility as photodynamic therapy (PDT) agents [8], and substrate binding and activation [9]. Recently, porphycenes have been used as functional building blocks incorporated into carbon nanomaterials [10].

Stable axial coordination in metalloporphyrin complexes has been convenient and powerful molecular approach to construct a novel series of redox- and photo-functional molecular assemblies, such as molecular wires via coordinative linkage [11]. Actually, the construction of well-defined, metalloporphyrin-based ensembles via axial coordination has constituted active research areas in the metallosupramolecular chemistry [12,13]. As a multicomponent molecular wire, Branda and the coworker have previously described [14] a linearly-arranged trinuclear ruthenium complex formulated as $[\text{Ru}(\text{TTP})(\text{CO})_2[\text{M}(\text{pytpy})_2]^{2+}$ (TTP = 5,10,15,20-tetratolylporphyrinato dianion; M = Ru and Os), in which two carbonyl-capped ruthenium(II)-porphyrin complexes are axially linked with a ruthenium(II)-bis(pytpy) complex.

In our current study, we have explored the synthesis of a new trinuclear molecular wire, **Chart 1**, by employing a ruthenium(II)-porphycene complex as an unprecedented molecular component: $[\text{Ru}(\text{TPrPc}(\text{CO}))_2[\text{Ru}(\text{pytpy})_2](\text{PF}_6)_2$ (**1**; TPrPc = 2,7,12,17-tetra-*n*-propylporphycenato dianion and pytpy = 4'-(4-pyridyl)-2,2':6',2''-terpyridine). This trinuclear complex represents the first example of molecular wires constructed from ruthenium(II)-porphycenes. This

paper reports the synthesis, spectroscopic characterizations, electrochemical properties, and photochemical properties of **1**.

Chart 1. Chemical Structure of the Trinuclear Molecular Wire **1**



Complex **1** was prepared by reacting 2 equiv. of $[\text{Ru}(\text{TPrPc}(\text{CO}))(\text{MeOH})]$ (**2**) [15,16] with $[\text{Ru}(\text{pytpy})_2](\text{PF}_6)_2$ (**3**) [17,18] in acetone for 24 h at room temperature and, after workup, isolated as a bluish green solid in a 58% yield [19]. The compound was fully characterized by various spectroscopic methods, mass spectrometry, and cyclic voltammetry. ¹H NMR spectroscopy (acetone-*d*₆) reveals the formation of the expected trinuclear structure comprised of $[\text{Ru}(\text{TPrPc}(\text{CO}))]$ and $[\text{Ru}(\text{pytpy})_2]^{2+}$ moieties in a 2:1 ratio. A noticeable ring current effect of the TPrPc²⁻ ligand is seen for a resonance due to 2,6-H of the pyridyl group in pytpy which appears at δ 1.18. ESI-MS shows a parent mass envelope at $m/z = 967.6$ with a peak interval of 0.5, indicating formation of the anticipated trinuclear complex with an overall charge of +2. In addition, an IR spectrum (KBr pellet) exhibits a strong $\nu(\text{CO})$ peak ascribed to the $[\text{Ru}(\text{TPrPc}(\text{CO}))]$ group at 1930 cm⁻¹ which is comparable with that of the monomeric precursor **2** (1932 cm⁻¹).

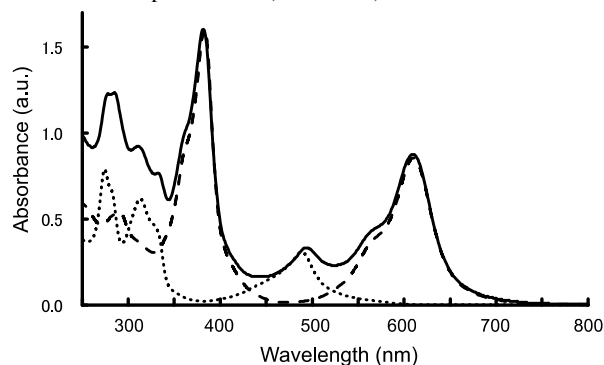


Figure 1. UV-vis absorption spectra of trinuclear complex **1** (solid line), $[\text{Ru}(\text{TPrPc}(\text{CO})(\text{pyridine}))]$ (**2'**, broken line), and $[\text{Ru}(\text{pytpy})_2](\text{PF}_6)_2$ (**3**, dotted line).

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The UV-vis spectrum of **1** in CH₂Cl₂, **Fig. 1**, shows absorption bands ascribed to two distinct monomeric components [Ru(TPrPc)(CO)] and [Ru(pytpy)₂]²⁺. Major absorptions include the Q-band ($\lambda_{\text{max}} = 640$ nm with a shoulder at 580 nm) and Soret band (384 nm with a shoulder at 360 nm) of the TPrPc²⁻ ligand as well as a metal-to-ligand charge transfer (MLCT) band ($\lambda_{\text{max}} = 495$ nm) due to [Ru(pytpy)₂]²⁺. The absorption pattern of **1** is thus very similar to the sum of absorption bands of a pyridine-coordinated ruthenium(II) porphycene [Ru(TPrPc)(CO)(pyridine)] (**2'**) [15,16] and **3** (**Fig. 1**), indicating that the electronic features for the individual chromophores in **1** remain almost unchanged upon coordinative linkage. According to a preliminary molecular modeling study, intermetallic distances over 1.0 nm were estimated for **1** [20]. Mutual orthogonality of the Ru^{II} d π and organic (TPrPc²⁻ and pytpy) p π components may also minimize the intramolecular electronic coupling.

Table 1. Electrochemical Data of **1** in 0.1 M *n*-Bu₄NPF₆-CH₂Cl₂.^{a)}

$E_{1/2}$ in V vs. Ag/AgCl (ΔE_p in mV)	Redox Process
-1.46 (80)	TPrPc ^{2-/-}
-1.29 (60)	(pytpy ⁻) ₂ /(pytpy ⁻)(pytpy)
-1.11 (70)	TPrPc ^{-/0}
-0.96 (50)	(pytpy ⁻)(pytpy)/(pytpy) ₂
+0.78 (80)	TPrPc ^{0/+}
+1.19 (80)	TPrPc ^{+/2+}
+1.44 (120)	Ru ^{II/III} (pytpy) ₂

a) Conditions: Working electrode = Pt. Counter electrode = Pt. Reference electrode = Ag/AgCl. Scan rate = 100 mV s⁻¹.

The redox property of **1** has been studied by cyclic voltammetry and the results are given in **Table 1**. Complex **1** (1.0 mM) shows consecutive electron-transfer processes in a 0.1 M *n*-Bu₄NPF₆-acetone solution at 298 K in the potential region between -1.60 and +1.60 V vs. Ag/AgCl. Four redox waves observed at $E_{1/2} = -1.46$, -1.11, +0.78, and +1.19 V are assigned to porphycene ring-centered processes, which is supported by comparison with electrochemistry of **2'** recorded under the same conditions ($E_{1/2} = -1.43$, -1.10, +0.83, and +1.23 V). The rest of two redox waves located in the negative potential region, $E_{1/2} = -1.29$ and -0.96 V, are therefore assigned to be pytpy ligand-centered. A quasi-reversible wave located in the most positive potential region, $E_{1/2} = +1.44$ V, is most likely ascribed to the metal-centered Ru^{II/III} process in the [Ru(pytpy)₂] unit. Here, two Ru(II) centers buried in the TPrPc²⁻ ligands are inactive to the redox event due to a significant stabilization of the divalent state by axial coordination of CO with a high π -accepting character.

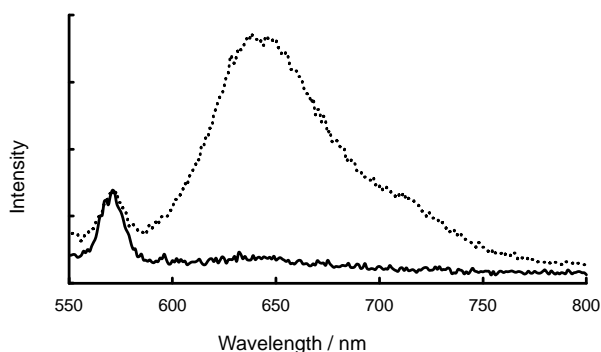


Figure 2. Emission spectra of the trinuclear complex **1** (solid line) and [Ru(pytpy)₂](PF₆)₂ (**3**, dotted line) in degassed acetone at 298 K. Excitation wavelength = 495 nm ($A_{495} = 0.01$).

Multicomponent metalloporphyrin arrays are of interest in the construction of molecular photonic wires [21]. In this context, the emission properties of **1** and mononuclear complex **3** have been examined. As shown in **Fig. 2**, complex **3** (dotted line) exhibits a broad and weak emission at 640 nm in acetone at 298 K upon excitation of the MLCT band at 495 nm. This is ascribed to phosphorescence from a low energy ³MLCT excited state [18]. Upon illumination at the same wavelength, trinuclear complex **1** (solid line) shows, in contrast, no phosphorescence in the identical wavelength region, indicating an entire quenching of the phosphorescence from the [Ru(pytpy)₂]²⁺ moiety. This quenching occurs as a result of axial binding of the porphycene groups to the emissive [Ru(pytpy)₂]²⁺ moiety. Plausible quenching pathways include an intramolecular energy transfer from the ³MLCT excited state of the [Ru(pytpy)₂]²⁺ moiety to the ³ π - π^* excited state of the terminal [Ru(TPrPc)(CO)] groups and ligand-induced quenching where the porphycene behaves as a Lewis acid [14]. Studies are in progress to more fully address the emission quenching mechanism for **1**.

In summary, we have described here a facile and convenient access to a redox-active molecular wire by employing a ruthenium(II)-porphycene complex as an unprecedented molecular building block. We have shown that, upon excitation of the MLCT band, the phosphorescence from the [Ru(pytpy)₂]²⁺ unit is completely quenched by the incorporation into the molecular wire backbone because of the acceptor ability of the axially-bound ruthenium(II)-porphycene groups. This work illustrates a remarkable utility of metalloporphycene complexes as new building blocks for molecular-scale photonic wires.

KEYWORDS: porphycene; ruthenium; molecular wire; cyclic voltammetry; luminescence

Received March 14, 2015; Accepted March 28, 2015

ACKNOWLEDGEMENT

This work was supported by Grants-in-Aid for Scientific Research on Innovative Areas "Molecular Activation" (No. 25105537) and "Coordination Programming" (No. 24108730), Grants-in-Aid for Scientific Research (A) (No. 21245016) and (B) (No. 25288031), the Global COE Program "Science for Future Molecular Systems", and Nanotechnology Platform (No. NPS13103) from MEXT. MA also acknowledges the financial support from Tokuyama Science Foundation. The authors thank Hiroki Futagawa for his assistance in preparing figures and table in this paper.

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19. A solution (1.4 mL) containing **2** (7.53 mg, 0.0118 mmol) and **3** (4.74 mg, 0.0074 mmol) in acetone was stirred for 24 h at room temperature and evaporated to dryness. The bluish green residue was dissolved in a minimal amount of dichloromethane, to which a mixture of diethyl ether/*n*-pentane (1:4, v/v) was added to precipitate **1**. The solid was collected by filtration and dried in vacuo. Yield: 6.1 mg (58%). Anal. Calcd for C₁₀₆H₁₀₂F₁₂N₁₆O₂P₂Ru₃: C, 57.21; H, 4.58; N, 9.97. Obsd: C, 57.21; H, 4.62; N, 10.07. ¹H NMR (500 MHz, acetone-*d*₆, 298 K) δ 1.38 (t, 24H, propyl CH₃), 2.41 (m, 16H, propyl CH₂), 4.09 (m, 16H, propyl CH₂), 8.90 (s, 8H, pyrrole-β), 9.74 (s, 8H, *meso*), 6.01 (d, 4H, pytpy), 6.91 (t, 4H, pytpy), 7.11 (d, 4H, pytpy), 7.73 (t, 4H, pytpy), 8.31 (s, 4H, pytpy), 8.41 (d, 4H, pytpy). ESI-MS: *m/z* = 967.6; calcd *m/z* = 968.3 for [M–2(PF₆)]²⁺. UV–vis (CH₂Cl₂) λ_{max}/nm: 611, 560 (sh), 489, 384, 360 (sh), 333, 313, 283, 275.
20. *d*[Ru(TPrPc)•••Ru(pytpy)] and *d*[Ru(TPrPc)•••Ru(TPrPc)] are estimated to be *ca.* 1.1 and 2.2 nm, respectively.
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