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Five-nuclear Complexes of Zinc (II) Phthalocyanine with Directly Linked Terpyridine Ligands

Mutsumi Kimura[a)]*, Takashi Hamakawa[a)], Tsuyoshi Muto[a)], Kenji Hanabusa[a)], Hirofusa Shirai[a)], and Nagao Kobayashi[b)]

a) Department of Functional Polymer Science, Faculty of Textile Science and Technology,
Shinshu University, Ueda 386-8567, Japan
b) Department of Chemistry, Graduate School of Science, Tohoku University,
Sendai 980-77, Japan

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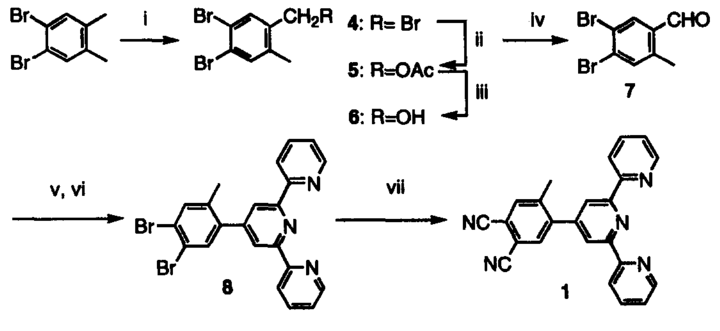
***Abstract*:** The synthesis of a novel ligand, in which four terpyridine groups are directly connected to a zinc (II) phthalocyanine unit, is described. Preliminary absorption, electrochemical, and fluorescence results are indicative of strong electronic coupling among the metal centers.

In recent years, there have been many attempts to construct organized artificial photosynthetic reaction centers made up of a discrete number of assembled photoactive molecular subunits.[1] Positioning photoactive subunits in close proximity to each other can result in strong electronic interaction between the components. These multicomponent photoactive systems have been achieved with covalent linkage and noncovalent bonding incorporating hydrogen bonds, coordination bonds, charge transfer interactions, and electrostatic attractive forces, and are shown to be effective photoinduced electron- and energy transfer reactions.[2] In this communication, we report here the synthesis, electrochemical properties, and luminescence behavior of a novel complex consisting of a zinc (II) phthalocyanine (ZnPc) and four bis(2, 2': 6', 2"-terpyridine)ruthenium (II) ($Ru(tpy)_2^{2+}$) linked by a single σ-bond.

Scheme 1



i, NBS, CCl_4; ii, AcOK, acetone, reflux, 48hr, 67%; iii, NaOH aq, reflux, 2h, 92%; iv, PCC, CH_2Cl_2, 80%; v, 2-acethylpyridine, KOH, MeOH; vi, 1-(2-pyridylcarbonylmethyl)pyridinum iodide, NH_4OAc, MeOH, reflux, 24hr, 46%; vii, CuCN, NMP, 78%.

The new phthalocyanine precursor **1** was prepared from 4,5-dibromxylene[3] according to Scheme 1. Bromination of 4,5-dibromo-xylene by N-bromo-

FAX: +81(268)21-7248, E-mail: mkimura@giptc.shinshu-u.ac.jp

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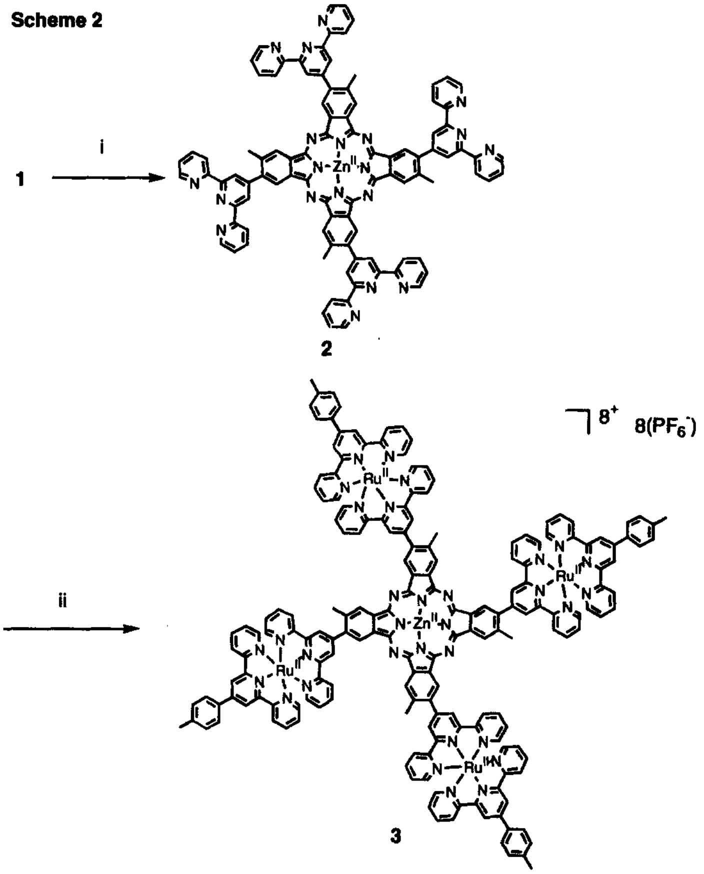
succinimide in CCl_4 gave the tribromoderivative **4**. Reaction of potassium acetate with **4** afforded **5** in 67% yield, and deacetylation of **5** proceeded in 92% yield. Compound **7** was obtained by oxidation of **6** with PCC in CH_2Cl_2 in 80% yield. The terpyridine ligand **8** was synthesized from **7** and 1-(2-pyridylcarbonylmethyl)pyridinium iodide according to literature procedure.[4] The phthalocyanine precursor **1** was obtained in 78% yield by reaction with CuCN in refluxed NMP.[5] Finally, cyclization of **1** in the presence of $ZnCl_2$ in 2,2'-dimethyl-aminoethanol gave **2** as a mixture of several positional isomers in 35% yield. The purification of **2** was achieved by column chromatography (basic alumina - DMF) and subsequent recrystallization (CH_2Cl_2 - hexane).[6]

Scheme 2



i, $ZnCl_2$, 2,2'-dimethylaminoethanol, reflux, 96hr, 35%; ii, Ru(MePh-tpy)(Cl)$_3$, $AgBF_4$, Acetone, DMF, reflux, 1hr, 40%.

The five-nuclear complex **3** was prepared as indicated in Scheme 2. The ruthenium complex was prepared according to the literature method.[7] After work-up, the crude brown-green product was purified by gel permeation chromatography on Biorad Biobeads SX-2 with acetonitrile as the solvent. After chromatography and anion exchange, the purity of five-nuclear complex **3** was checked by thin-layer chromatography, UV-visible spectroscopy and ^1H NMR spectroscopy.[8]

The electronic spectrum of **3** shown in Fig. 1 exhibits the characteristic absorption bands of ZnPc at 350nm (Soret band), 629nm and 692nm (Q bands), and the $Ru(tpy)_2^{2+}$ at 312nm (ligand centered), 494nm

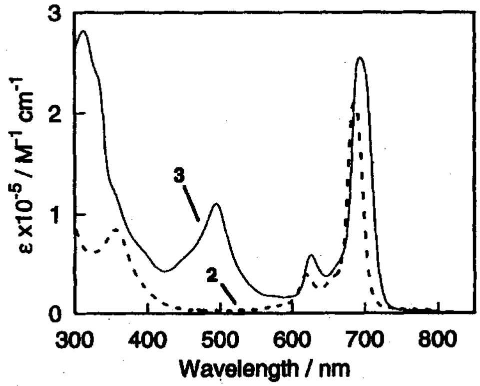


Figure 1. Absorption spectra (room termperature, DMF solution) of **2** and **3**.

(Ru-to-ligand charge transfer envelop). The molar absorption coefficient of the Ru-to-ligand charge transfer for **3** (logε = 5.07) was *ca.* four times that for bis[4'-(p-toly)-2, 2': 6', 2"-terpyridyl]-ruthenium(II) dihexafluorophosphate ($Ru(MePh\text{-}tpy)_2^{2+}$) (logε = 4.47) as a reference compound. The Q band of **3** exhibits a substantial red-shift from **2** lacking Ru complexes (λ_{max} = 684nm).

Table 1. Half-wave potentials of the 2 and 3 in DMF[a]

Complex	$E^{1/2}$ (ZnPc(-2)/ZnPc(-1))	$E^{1/2}$ ($Ru(tpy)_2^{2+/3+}$)
2	+0.57	
3	+0.55	+0.84
$Ru(MePh\text{-}tpy)_2^{2+}$		+1.03

[a] Redox poentials in dry DMF determined by cyclic voltametry (CV): $E^{1/2}$(approximated by $(E^a_p\text{-}E^c_p)/2$) in V vs. SCE; Pt working electrode, scan rate = 50mV/sec.

The results of electrochemical studies of these complexes provided useful information regarding the electronic condition. The complexes were investigated by using cyclic voltammetry in dry DMF containing 0.3M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte (Table 1). Compounds **2** and **3** yielded an oxidation wave at approximately +0.55V vs. SCE, typical value for phthalocyanine ring oxidation, whereas **3** yielded a one reversible oxidation wave at +0.84V vs. SCE as expected for the $Ru(tpy)_2^{2+/3+}$ couple. The oxidation potential of the $Ru(tpy)_2^{2+/3+}$ couple in **3** is more negative than that of the mononuclear complex $Ru(MePh\text{-}tpy)_2^{2+}$ because of the connection with the highly conjugated phthalocyanine ring. The electrochemistry of **3** indicates electronic interactions between the components. In order to assign the observed cyclic voltammetric signals to redox reactions of **3**, spectroelectrochemical studies were performed at a platinum grid working electrode. The absorption spectrum of **3** at +0.70V vs. SCE displayed a red shift for the Q band of the ZnPc moiety and the appearance of a new absorption band around 520nm. This spectral change is characteristic of the phthalocyanine ring oxidation from ZnPc(-2) to ZnPc(-1).[9]

Zinc(II) phthalocyanine complex **2** exhibits a strong fluorescence peak at 692nm with excitation at 370nm in degassed DMF solution at room temperature. The emission is shifted to 705nm in the five-nuclear complex **3**, and the relative fluorescence intensity is diminished due to the presence of $Ru(tpy)_2^{2+}$. This fluorescence behavior also shows the strong intramolecular electronic coupling between ZnPc and $Ru(tpy)_2^{2+}$. Interestingly, the ZnPc emission is observed from **3** with excitation at the MLCT band (λ_{max} = 494nm) of $Ru(tpy)_2^{2+}$ (Fig. 2). Mixtures, 1:4 and 1:100, of **2** and $Ru(MePh\text{-}tpy)_2^{2+}$ do not indicate any emission peak under the same conditions. It is well known that the $Ru(tpy)_2^{2+}$ has a short excited-state lifetime (≤20ps) and a weak luminescence intensity in fluid solution at room temperature.[10] Thus, the emission from **3** with excitation of the MLCT band is the result of the fast energy transfer from $Ru(tpy)_2^{2+}$ to ZnPc. The mechanism of this intramolecular energy transfer process is currently under investigation.

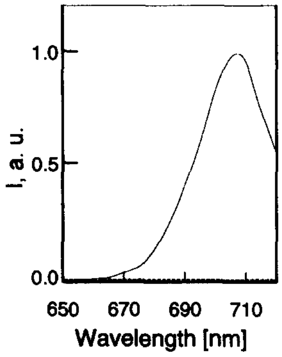


Figure 2. Luminescence spectra (room temperature, DMF solution, λ_{exc} 494nm) of **3** (—— , $[3]=1.0x10^{-6}M$) and **2**+$Ru(MePh\text{-}tpy)_2^{2+}$ (------ , $[2]=1.0x10^{-6}M$, $[Ru(MePh\text{-}tpy)_2^{2+}]=1.0x10^{-4}M$).

In summary, we have constructed a novel zinc (II) phthalocyanine complex bearing four $Ru(tpy)_2^{2+}$

linked by a single σ-bond. Analyses of the absorption spectra, electrochemistry, and luminescence properties of **3** show strong electronic interaction between the two components.

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5. *Selected data* for **1**: FT-IR (KBr): 2232cm^{-1} (CN); ^{1}H-NMR (CDCl$_3$, 25°C, 400MHz): δ = 8.72-8.64 (m, 4H, pyridine), 8.42 (s, 2H, pyridine), 7.86 (t, 2H, pyridine), 7.79 (s, 1H, Ph), 7.74 (s, 1H, Ph), 7.32 (t, 2H, pyridine), 2.46 (s, 3H, CH$_3$); Elemental analysis calculated for $C_{24}H_{15}N_5$: C, 77.2, H, 4.1, N, 18.7; Found: C, 77.1, H, 4.0, N, 18.5; EI-MS m/z = 373.1(**1** requires 373.42).
6. *Selected data* for **2**: ^{1}H-NMR (DMSO-d_6, 25°C, 400MHz): δ = 8.72-8.40 (m, 24H, pyridine), 7.96-7.70 (m, 16H, pyridine, Pc), 7.39 (s, 8H, pyridine), 2.73 (s, 12H, CH$_3$); FAB-MS (nitrobenzyl alcohol matrix): m/z = 1559.0 (**2**+H$^+$ requires 1559.05).
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8. *Selected data* for **3**: H-NMR (DMSO-d_6, 25°C, 400MHz): δ = 9.97-9.48 (m, 16H, pyridine, Pc), 9.23-9.13 (m, 8H, pyridine), 8.98-8.77 (m, 16H, pyridine), 8.42(m, 16H, pyridine), 8.20-8.00 (m, 16H, pyridine), 7.82(d, 8H, Ph), 7.71-7.38 (m, 24H, pyridine, Ph), 2.55 (s, 12H, CH$_3$), 2.50(s, 12H, CH$_3$); Elemental analysis calculated for $C_{184}H_{128}N_{32}P_8F_{48}ZnRu_4$: C, 50.0, H, 2.9, N, 2.9; Found: C, 49.6, H, 3.1, N, 2.8.
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