Synthesis of Multicomponent Systems Composed of One Phthalocyanine and Four Terpyridine Ligands

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Two phthalocyanine-based multiple ligands were synthesized and characterized. Photochemical and electrochemical properties were measured for zinc(II) phthalocyanines covalently linked with four ruthenium(II) bisterpyridyl complexes. The absorption and electrochemical results are indicative of electronic interaction between two photoactive and redox-active components. Fluorescence spectroscopy of the five nuclear complexes provides evidence of an efficient photoinduced intramolecular energy transfer between the ruthenium-based metal-to-ligand charge-transfer (MLCT) chromophores and the zinc(II) phthalocyanine core. The absorption and fluorescence spectra of the phthalocyanine-based multiple ligands change dramatically as a result of the coordination of metal ions with peripheral terpyridine ligands. This change of fluorescence intensity upon addition of metal ions can apply to an output signal for metal ion sensing. The direct attachment of metal ion receptors with a zinc phthalocyanine core enhanced efficiency of the energy- and electron-transfer reaction from the core to the metal complexes.

Introduction

The design and synthesis of multicomponent systems containing discrete redox-active and photoactive units have attracted much attention because of their potential for the fabrication of nanoscopic electronic and photonic devices.[1] In these systems, the functional molecular units were assembled through covalent bonds and noncovalent interactions such as hydrogen bonding, metal−ligand interactions, and donor−acceptor interactions.

Assembly of metal complexes (metallosupramolecules) has been investigated actively because of their attractive electronic, magnetic, catalytic, and photonic properties.[2] Polypyridyl ligands have been widely used for the construction of highly ordered organic−inorganic hybrid architectures such as dyads, triads, coordination polymers, wires, rods, helicates, catenanes, knots, macrocycles, and dendrimers.[3−9] Sauvage, Balzani, Barigelletti, and their co-workers have investigated integrated molecular systems containing metal complexes.[10] The heteronuclear complexes having ruthenium(II) and osmium(II) metal centers exhibited fast energy transfer.[11] The design of multiple ligands allows a directional and effective electron and energy transfer.

Phthalocyanines and their metal complexes have two strong absorption bands located in the far-red end (Q-band) and the blue (Soret band) of the visual region. The construction of multicomponent systems based on phthalocyanines with other red chromophores may convert a large part of the solar spectrum.

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While porphyrin-based multicomponent systems have been developed,[12] the attachment of photoactive and redox-active moieties to the phthalocyanine macrocycle has not been as extensively explored. Phthalocyanine-based multicomponent systems containing porphyrin, ferrocene, tetrathiafulvalene, sterically hindered phenol, and C_{60} have been reported.[13−17] Very recently, star-shaped multiporphyrin−phthalocyanine conjugated arrays have been prepared by Lindsey et al.[18]

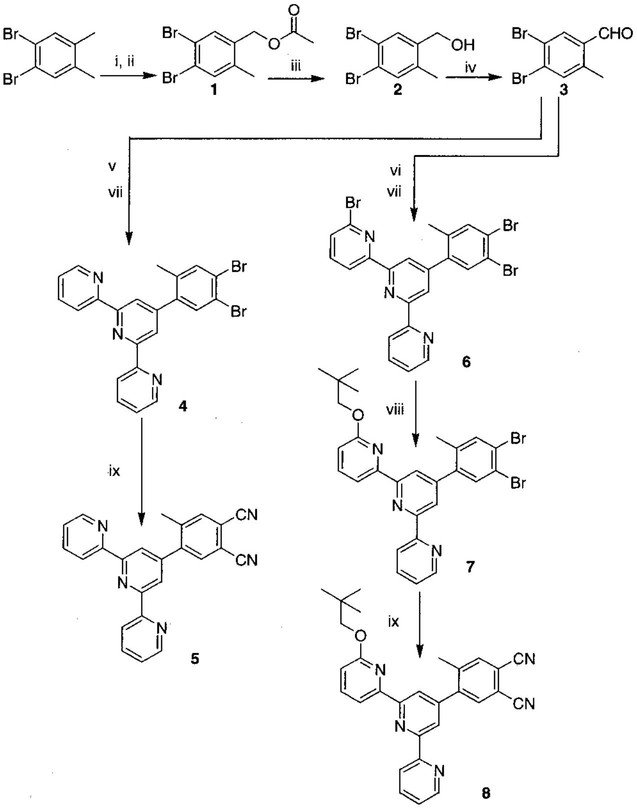
In this study, we report the synthesis of two novel phthalocyanine-based multiple ligands, in which four terpyridine units were directly attached to a phthalocyanine, as well as their five-nuclear complexes containing four ruthenium(II) bis(terpyridine) complexes ($Ru(tpy)_2^{2+}$) and one zinc(II) phthalocyanine complex (ZnPc).[19] The ruthenium complex $Ru(tpy)_2^{2+}$ has a broad absorption band at ca. 490 nm, which is located between the Q-band and the Soret band of the phthalocyanine moiety.[11] We expected strong electronic interaction between the phthalocyanine moiety and the ruthenium complexes via a single σ-bond and an efficient excited-state energy transfer in the five-nuclear complexes. Furthermore, the terpyridine units act as an excellent receptor for many metal ions. We also demonstrate the sensing ability of multiple ligands for metal ions by the change of fluorescence.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Bruker AVANCE 400 FT-NMR spectrometer operating in $CDCl_3$ solution at 400.13 MHz for ^1H. Chemical shifts were relative to internal TMS. Elemental analyses were performed with Perkin-Elmer series II CHNS/O analyzer 2400. IR spectra were obtained on a JASCO FS-420 spectrometer as KBr pellets. Mass spectra of phthalocyanins and multinuclear complexes were obtained by matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy or by high-resolution fast atom bombardment (FAB). MALDI-TOF mass spectra were obtained on a PerSeptive Biosystems Voyager DE-Pro spectrometer with dithranol as matrix.

Absorption and Emission. UV−vis and fluorescence spectra were recorded on a JASCO V-570 and a JASCO FP-750. Emission quantum yields of the phthalocyanines in multinuclear complexes were measured by comparison of emission spectra using $(t\text{-Bu})_4ZnPc$ ($\Phi_F = 0.20$) as the standard with excitation at 356 nm.

Scheme 1[a]



[a] (i) NBS, CCl_4; (ii) AcOK, acetone, reflux, 48 h; (iii) NaOH aq, reflux, 2 h; (iv) PCC, CH_2Cl_2; (v) 2-acetylpyridine, KOH, MeOH; (vi) 2-acetyl-6-bromopyridine, KOH, MeOH, (vii) 1-(2-pyridylcarbonylmethyl)pyridinium iodide, NH_4OAc, MeOH, reflux, 24 h; (viii) $(CH_3)_3CCH_2OH$, NaH, DMF; (ix) CuCN, NMP, 180 °C.

Electrochemisty. Electrochemical measurements were carried out at room temperature with an ALS/CHI model 400. The cyclic voltammetric experiments (CV) were performed in a 1.0 mL cell equipped with a Pt counter electrode, a Ag/AgCl reference electrode, and a Pt electrode (0.0177 cm^2). The complexes were dissolved in degassed dry DMF containing *n*-tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Aldrich) as the supporting electrolyte (0.10 M). The concentration of the complexes was 5×10^{-4} M. Prior to its use, $TBAPF_6$ was purified by recrystallization three times from ethyl acetate and dried under vacuum for 48 h. Dry nitrogen was bubbled through solutions for 5 min before CV experiment. For the reversible processes, half-wave potentials (vs SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks, the close-to-unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. In situ UV−vis spectra of multinuclear complexes at different applied potentials were recorded in a quartz cell (1.0 cm × 1.0 cm) equipped with a Pt counter electrode, a Ag/AgCl reference electrode, and a Pt mesh electrode (80 mesh).

Results and Discussion

Synthesis of Ligands. The phthalocyanine precursors **5** and **8** were synthesized from 4,5-dibromoxylene[20] as a starting material by seven- and eight-synthetic-step processes, respectively (Scheme 1). One CH_3 group in 4,5-dibromoxylene was converted into a CH_2Br by *N*-bromosuccinimide (NBS) in CCl_4. Reaction of the CH_2Br group with potassium acetate affords **1**.

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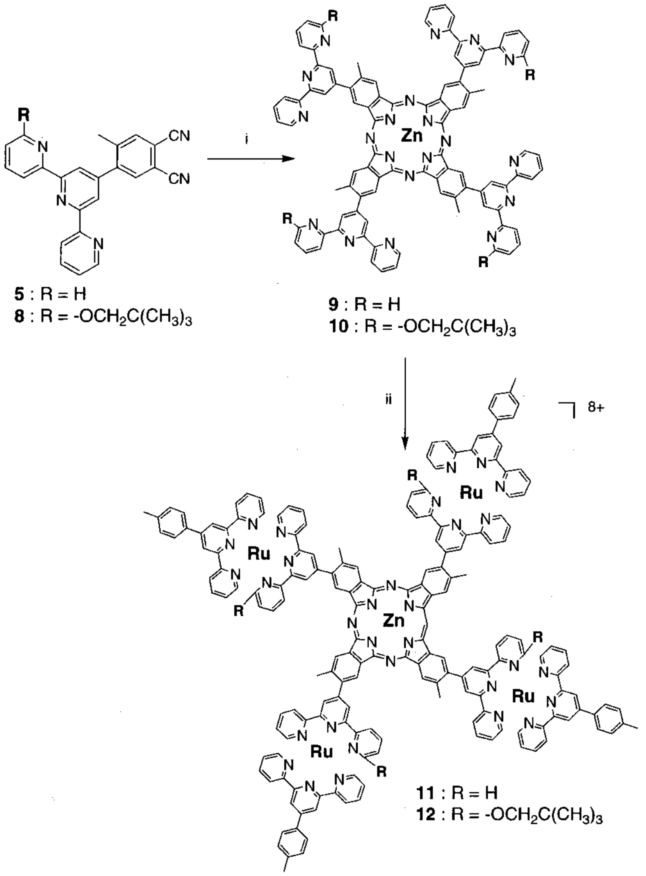
Scheme 2[a]



[a] Compounds **9**−**12** are composed of a mixture of regioisomers. (i) $ZnCl_2$, 2,2′-dimethylaminoethanol, reflux, 96 h; (ii) Ru(MePh-tpy)$(Cl)_3$, $AgBF_4$, acetone, DMF, reflux, 1 h.

After hydrolysis of the acetyl group, 4,5-dibromo-2-methylbenzaldehyde, **3**, was obtained by the oxidation of **2** with pyridinium chlorochromate (PCC). Two terpyridine ligands were prepared according to the Kröhnke method.[21] The ligands **4** and **6** were obtained by the reaction of 1-(2-pyridylcarbonylmethyl)pyridinium iodide with enone derived from **3** and 2-acetylpyridine or 2-acetyl-6-bromopyridine, respectively, in the presence of ammonium acetate. The substituted terpyridine, **7**, was obtained from the reaction of **6** with the sodium salt of 2,2-dimethyl-1-propanol by using Constable methodology.[22] The synthesized ligands **4** and **6** were isolated as white solids and were fully characterized by ^1H NMR, mass spectroscopy, and elemental analyses. In the final step, a Rosenmund−Von Braum reaction yielded the dicyanides **5** and **8**, which were converted into the corresponding ZnPc **9** and **10** by refluxing in 2-(dimethylamino)ethanol in the presence of $ZnCl_2$ (Scheme 2).[23] After purification with column chromatography, ca. 35% of pure products were isolated. While **9** was soluble only in DMF, **10** was highly soluble in $CHCl_3$, toluene, THF, and pyridine. The introduction of neopentoxy groups at the 6 position of terpyridine moieties improved solubility of phthalocyanine-based multiple ligands for organic solvents. ^1H NMR spectra of **9** and **10** showed multiple peaks from the aromatic protons for the phthalocyanine moiety, indicating the presence of four possible regioisomers.

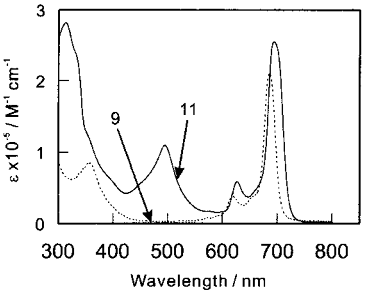


Figure 1. Absorption spectra of **9** and **11** in DMF at room temperature.

Synthesis of Complexes. The five-nuclear complexes **11** and **12** were prepared according to the literature procedures (Scheme 2).[11] The terpyridyl ligands can form bis(terpyridyl) metal complexes by the addition of six-coordinate metal ions. The geometry of bis(terpyridyl) metal complexes allows the assembly of two different terpyridine ligands through a stepwise synthetic procedure. The terminated 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine (Meph-tpy) reacted with $RuCl_3$ and yielded Ru(Meph-tpy)Cl_3. After dechlorination of the Ru(Meph-tpy)Cl_3, the five-nuclear complexes **11** and **12** were obtained by the reaction of excess labile solvated ruthenium precursor (Meph-tpy)Ru$(acetone)_3^{2+}$ with **9** and **10**, respectively. After size exclusion chromatography and anion exchange, the purity was checked by HPLC, ^1H NMR, UV−vis, mass spectroscopy, and elemental analysis.

Photophysical and Electrochemical Properties. The absorption spectra of the novel phthalocyanine-based multiple ligand, **9**, and its five-nuclear complex, **11**, are shown in Figure 1, and the absorption maxima (λ_{max}) and molar absorption coefficients (ϵ) of all compounds, **9**−**12**, and reference compounds are collected in Table 1. The absorption spectrum of **9** showed a sharp strong peak at $\lambda_{max} = 684$ nm ($\epsilon = 1.7 \times 10^5$ M^{-1} cm^{-1}) and a relatively weak peak at $\lambda_{max} = 350$ nm as the Q-band and the Soret band of the phthalocyanine core in **9**.[24] In addition to the Q-band and Soret band for the ZnPc core, the five-nuclear complex, **11**, exhibits ligand-centered (LC) and metal-to-ligand charge-transfer (MLCT) features corresponding to the $Ru(tpy)_2^{2+}$ complex. The molar absorption coefficient value for the MLCT band for **11** was ca. 4 times that for the reference compound Ru(Meph-tpy)$_2$$(PF_6)_2$. Moreover, the Q-band in **11** is red-shifted and slightly broadened compared with **9**, which may indicate that the direct connection of $Ru(tpy)_2^{2+}$ complexes with the ZnPc core allows some intercomponent electronic interaction. The five-nuclear complexes **11** and **12** can absorb a large part of the solar spectrum from 350 to 700 nm.

Electrochemical studies were performed in dry DMF solution containing $TBAPF_6$ (0.1 mol L^{-1}) as the supported electrolyte. The electrochemical results for **9**−**12** are also gathered in Table 1. Without Ru-based moieties, **9** and **10** only show one reversible oxidation couple at +0.57 V (vs SCE),[25] while the

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Table 1. Photophysical and Electrochemical Data for **9**−**12**

	λ_{max}, nm (log ϵ, M^{-1} cm^{-1})^a		E (vs SCE)^b		
compound	MLCT	Q-band	$Ru^{2+/3+}$	ZnPc(−2)/ZnPc(−1)	λ_{em}, nm (Φ_F)^c
9		620 (4.52), 684 (5.32)		+0.57	692 (0.22)
10		620 (4.53), 688 (5.28)		+0.58	693 (0.21)
11	494 (5.07)	626 (4.77), 692 (5.42)	+0.89	+0.55	705 (0.05)
12	496 (5.06)	626 (4.75), 692 (5.43)	+0.84	+0.56	706 (0.05)
Ru(Meph-tpy)(PF_6)$_2$^{d}	490 (4.46)		+1.08		650

^{a} DMF solution, room temperature. ^{b} Dry DMF solution containing 0.1 M $TBAPF_6$, room temperature. ^{c} Deaerated DMF solution. ^{d} Reference 11.

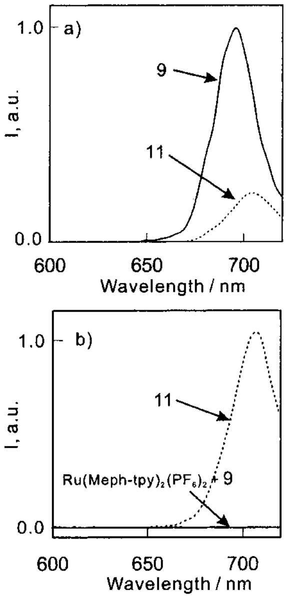

Figure 2. Fluorescence spectra of **9** and **11** in deaerated DMF at room temperature with excitation at the Soret band (370 nm) (a) and the MLCT band of $Ru(tpy)_2^{2+}$ (494 nm) (b) ([**9**] = [**11**] = 1.0 μM). The solid line in Figure 2b is the fluorescence spectrum of the mixture of **9** and Ru(Meph-tpy)$_2$(PF_6)$_2$ ([**9**] = 1.0 μM, [Ru(Meph-tpy)$_2$(PF_6)$_2$] = 0.1 mM).

five-nuclear complexes **11** and **12** show two reversible oxidation processes at +0.55 and +0.89 V (vs SCE). To assign the observed cyclic volammetric signals to redox reactions of **11**, in situ UV−vis spectra of **11** at different applied potentials were performed at a platinum grid working electrode. The absorption spectrum of **11** at +0.70 V displayed a red shift for the Q-band and the appearance of a new absorption band around 520 nm. This spectral change is characteristic of the phthalocyanine ring oxidation from ZnPc(−2) to ZnPc(−1).[26] The oxidation potentials of the ZnPc core in **9** and **11** remained almost intact. On the other hand, the second redox couple at +0.89 V, which was assigned as the oxidation process for the $Ru^{2+/3+}$ redox couple, was more negative than that of the reference compound Ru(Meph-tpy)$_2$(PF_6)$_2$. This is due to the direct connection of the highly conjugated phthalocyanine core on the side of the Ru-based moiety. This electrochemical behavior agrees with the result previously reported by Sauvage et al. on porphyrin−Ru(tpy)$_2$ trinuclear complexes.[27a]

Fluorescence Properties. The emission spectra at room temperature of **9** and **11** are shown in Figure 2. Compound **9** exhibited a strong fluorescence at 692 nm (Φ_F = 0.22) upon excitation at the Soret band of the phthalocyanine core (Figure 2a). In contrast, the emission shifted to 705 nm in **11**, and the relative fluorescence intensity diminished 4.4-fold (Φ_F = 0.05) compared with that of **9**. Upon excitation of **11** and **12** at 494 nm, where only the Ru(tpy)$_2$ moieties absorbed, fluorescence was exclusively from the phthalocyanine core (Figure 2b). Mixtures at ratios of 1:4 and 1:100 of **9** and Ru(Meph-tpy)$_2$(PF_6)$_2$ did not indicate any emission peak upon excitation at the MLCT band for Ru(Meph-tpy)$_2$(PF_6)$_2$. The excited-state lifetime of $Ru(tpy)_2^{2+}$ complex is short (<20 ps), and the Ru(tpy)$_2$ complex emitted only a weak fluorescence in fluid solution at room temperature.[27] These results indicate a very efficient photoinduced intramolecular energy transfer from $Ru(tpy)_2^{2+}$ moieties to the ZnPc core.

Sensing Ability for Metal Ions. The integration of receptors with chromophores and fluorophores has been shown to develop highly efficient chemosensor responses to target analytes.[28] Many attempts at the design and construction of chemosensors using optical, fluorescence, and redox changes as output signals have been reported.[29] The oligopyridine ligands possess an excellent ability to coordinate a large number of metal ions, and these ligands have been utilized as a receptor in chemosensors for metal ions. In this context, we demonstrate sensing ability of the synthesized phthalocyanine-based multiple ligands **9** and **10** by using the change of fluorescence behavior on the addition of several kinds of metal ions.

The absorption spectrum of **9** changed upon the addition of Fe^{2+} ion, and a new band at 568 nm appeared (Figure 3a). When the Fe^{2+} concentration increased, the intensity corresponding to the Q-band of the phthalocyanine core decreased and red-shifted. It is well-known that tpy ligands and Fe^{2+} ion form a very stable low-spin $Fe(tpy)_2^{2+}$ complex and $Fe(tpy)_2^{2+}$ complex shows a characteristic MLCT band around 570 nm.[30] In contrast, the appearance of the MLCT band was not observed in **10** upon addition of Fe^{2+} ion (Figure 3b). The introduction of substituents in the 6 positions of the tpy ligands led to the formation of a high-spin complex on reaction with Fe^{2+} ion.[31] Constable et al. reported the solid-state X-ray structures of $Fe(tpy)_2^{2+}$ complexes

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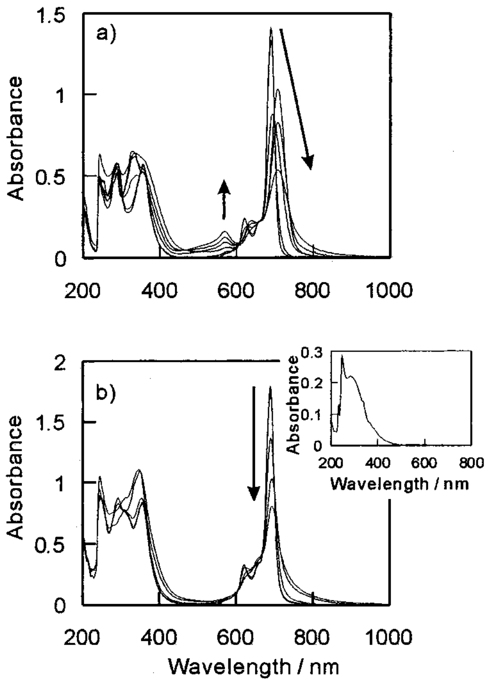

Figure 3. Effect of Fe^{2+} concentration on the absorption spectrum of **9** (a) and **10** (b) in CHCl$_3$−MeOH: [**9**] = [**10**] = 1.0 μM, [Fe^{2+}] = 0, 0.2, 0.4, 0.6, 0.8, 1.0 μM. Arrows indicate the direction of the spectral change. The inset shows the absorption spectrum of Fe(**8**)$_2$(PF$_6$)$_2$ in acetonitrile.

with 4,6-diphenyl-2,2′:6′,2″-terpyridine ligands.[31b] This complex has a distorted structure because of the steric strain in the assembly of two tpy ligands with one Fe^{2+} ion. The absorption spectrum of Fe(**8**)$_2$(PF$_6$)$_2$ was transparent at the MLCT band as shown in the inset of Figure 3b. The absorption spectrum of Fe(**8**)$_2$(PF$_6$)$_2$ was very similar to the reported spectra of high-spin Fe(tpy)$_2$ complexes.[30b] The ligand **8** and the phthalocyanine-based multiple ligand **10** having neopentoxy groups at 6 positions of tpy ligands also formed high-spin Fe(tpy)$_2$ complexes with the addition of Fe^{2+} ion. While the brown precipitate formed over half of the concentration of **9**, **10** was still soluble upon addition of over 10-fold concentration of Fe^{2+} ion. The MALDI-TOF mass spectrum of the isolated complex after mixing **10** with excess FeCl$_2$ showed an ion peak at 2370.3, indicating the formation of a 1:1 complex between the tpy ligand in **10** and Fe^{2+} ion (**10** + 4Fe^{2+} + 7Cl$^-$). Furthermore, the absorption and emission spectra of the mixture of **10** with excess Fe^{2+} ion recovered into those of Fe^{2+}-free **10** when ammonia gas was bubbled for 1 min. The iron complex of **10** with FeCl$_2$ was easily decomposed by the ligand substitution reaction. On the other hand, the spectral change in **9** was not observed after bubbling with ammonia gas. This observation also reflects the difference in the electronic configuration for the resulting Fe^{2+} complexes. The ligand **10** was superior to **9** as a chemosensing material for metal ions because of its high solubility in the wide range of metal ion concentrations.

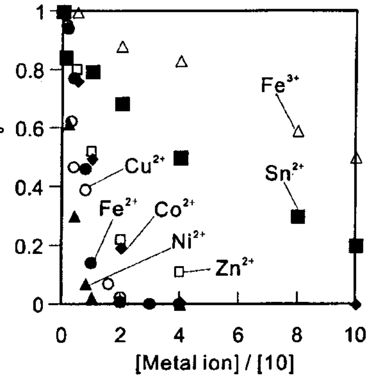

Figure 4. Relationship between the relative fluorescence intensity of **10** ([**10**] = 1.0 μM) in CHCl$_3$/MeOH and the addition of added metal ions (λ_{ex} = 370 nm, λ_{em} = 700 nm).

The fluorescence emission from **10** was monitored as several transition metal ions (Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Sn^{2+}, and Zn^{2+}) were titrated into a solution of **10** in degassed CH$_2$Cl$_2$/methanol mixture. The addition of Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+} to the solution of **10** led to efficient fluorescence quenching, and the profile of the fluorescence quenching depended on the kind of metal ion (Figure 4). In contrast, the fluorescence intensity of **10** gradually was decreased by Fe^{3+} and Sn^{2+}. Tetrakis(*tert*-butyl)phthalocyaninato zinc(II) complex ((t-Bu)$_4$ZnPc), lacking receptor sites for metal ions, showed no change in the absorption and emission spectra for all metal ions tested. The phthalocyanine-based multiple ligand **10** displayed an excellent sensing ability for metal ions, responding to different concentrations and kinds of metal ions. Association of tpy units in **10** with metal ions enhanced the efficiency of the energy or electron transfer between the ZnPc core and receptor sites.

Conclusion

We have synthesized new multiple ligands and five-nuclear complexes possessing one ZnPc and four tpy units. These components were directly connected with a single σ-bond. Analyses of the absorption spectra, electrochemistry, and fluorescence properties of the five-nuclear complexes show an intercomponent electronic interaction. These complexes can absorb a large part of the solar spectrum from 350 to 700 nm and convert a large part of the solar spectrum through efficient photoinduced energy transfer. The direct connection of tpy ligand with ZnPc also enabled sensing for metal ions as well as monitoring fluorescence of ZnPc on the addition of metal ions. The design of artificial supramolecular systems based on the direct assembly of chromophores and fluorophores may permit controlled transformation of molecular information and provide the opportunity to construct molecular-based electronic and photonic devices.

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Supporting Information Available: Synthesis and characterization of new compounds **1**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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