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Charge-Transfer Complexation and Photoreduction of Viologen Derivatives Bearing the Para-Substituted Benzophenone Group in Dimethyl Sulfoxide

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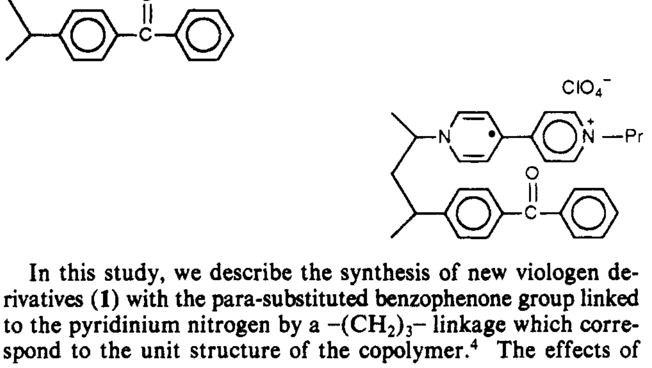
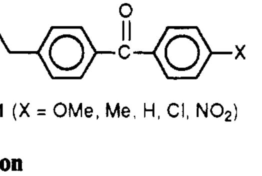
New viologen derivatives having the various para-substituted benzophenone groups connected with a $-(CH_2)_3-$ linkage were effectively photoreduced by dimethyl sulfoxide by the intramolecular charge transfer complex formation between the viologen and benzophenone groups through effective stacking. The photoreduction was enhanced by the introduction of electron-donating para-substituents on the benzophenone units which were favorable for the intramolecular charge transfer complexation.

Introduction

Viologens (V^{2+}) have been widely studied as electron-transfer catalysts for the reduction of proton[1] and some organic compounds.[2] Especially, photoreduction of viologen by 2-propanol sensitized by benzophenone[3] have been investigated to convert photoenergy into chemical energy. We have already reported[4] that copolymers with the viologen and benzophenone groups linked directly to main chain have exhibited charge-transfer complexation between both groups through effective stacking in the copolymer, by working viologen as an acceptor and benzophenone as a donor. We have also found[4] that the photoreduction of these viologen copolymers have proceeded by an aprotic solvent, dimethyl sulfoxide (DMSO), as a reducing agent for the first time.



In this study, we describe the synthesis of new viologen derivatives (**1**) with the para-substituted benzophenone group linked to the pyridinium nitrogen by a $-(CH_2)_3-$ linkage which correspond to the unit structure of the copolymer.[4] The effects of substituents on the interaction between the viologen and benzophenone groups of derivatives **1** and on the photoreduction of **1** to the viologen cation radical ($V^{\bullet+}$) are also investigated.



1 (X = OMe, Me, H, Cl, NO_2)

Results and Discussion

Viologens having various para-substituted benzophenone groups with the $-(CH_2)_3-$ linkage were synthesized as shown in eq 1.

The effect of para substituent on the intramolecular interaction was investigated by measuring the electronic spectra of viologen derivatives in DMSO, one of the solvents of high donor number. Viologen derivatives with the para-substituted benzophenone group, **1a**, **1b**, **1d**, and **1e** showed a visible absorption (λ_{max} ca. 480 nm) as well as the unsubstituted derivative **1c** (Figure 1). The absorptions disappeared by addition of perchloric acid in every case. The visible absorption was not observed in the intermolecular system of propyl viologen diperchlorate (PrV^{2+}) and the corresponding para-substituted benzophenones. From these results, the intramolecular charge transfer complexation assisted by the solvent was suggested between the viologen and benzophenone groups which were suitably situated to stack each other in derivatives **1**, as also reported in the copolymer system.[5] As for **1e** with the NO_2 substituent, a visible absorption was very weak compared to the other derivatives. In this case, the charge donation

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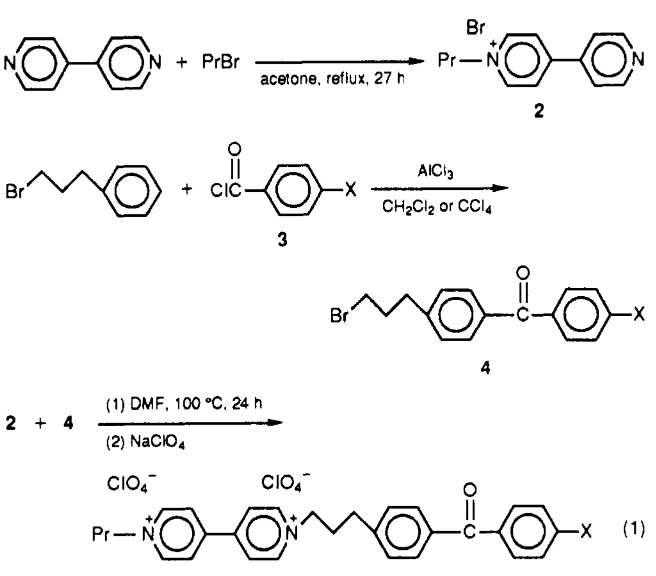


1a: X = MeO
1b: X = Me
1c: X = H
1d: X = Cl
1e: X = NO$_2$

of benzophenone moiety to the viologen moiety was decreased by the electron-withdrawing NO$_2$ substituent.

Photoreduction of **1** in DMSO was carried out by irradiation with xenon lamp ($\lambda > 350$ nm). The solution turned to deep blue in every case and the electronic spectrum showed the absorption at 610 nm corresponding to the $V^{\bullet+}$ (Figure 2). Conversion of **1a–e** to $V^{\bullet+}$ by photoirradiation was estimated from Figure 2 and plotted against the irradiation time in Figure 3. The photoirradiation of **1a**, **1b**, and **1d** gave $V^{\bullet+}$ effectively in the conversions of 19, 22, and 21% for 140 min, respectively, which were higher than that of the unsubstituted **1c** (12%). On the other hand, photoreduction of intermolecular systems of PrV^{2+} and the corresponding para-substituted benzophenones in DMSO gave only the 2–3% of $V^{\bullet+}$, similar to the photoreduction of **1e** itself (3%).

Thus, the effective photoreduction was observed when the electron-donating para substituents (mainly due to mesomeric effect) such as methoxy, methyl, and chloride groups were introduced into the benzophenone unit. Also in these cases, the strong interaction between the viologen and benzophenone parts was confirmed by the charge-transfer complexation.

The monochromatic photoirradiation of viologen derivatives **1b**, **1c**, and **1d** was investigated in DMSO to clarify the substituent effect. The $V^{\bullet+}$ conversions of **1d** for various irradiation wavelengths were plotted against the photoirradiation time (Figure 4). By irradiation at 312 nm the $V^{\bullet+}$ once produced was decomposed rapidly. As Ledwith et al.[6] postulated in the photobleaching of methyl viologen cation radical, the decomposition of $V^{\bullet+}$ would be caused by the photoreaction of the $V^{\bullet+}$ with the benzophenone ketyl radical to produce a dihydro derivative of viologen on irradiation with the light of shorter wavelengths. The $V^{\bullet+}$ conversion of these derivatives irradiated for 30 min against the irradiation wavelength was plotted in Figure 5. Irrespective of the substituents, the maximum $V^{\bullet+}$ conversion was obtained by the irradiation at 365 nm, corresponding to the n–p* band of the carbonyl group of benzophenone derivatives. These tendencies were unchanged by normalization with the relative light intensities cited in the Experimental Section. Therefore, it was suggested that the photoreduction of viologen proceeds not by the excitation of the charge-transfer band (around 480 nm) but by the excitation of the n–p* transition of carbonyl group in the benzophenone part.

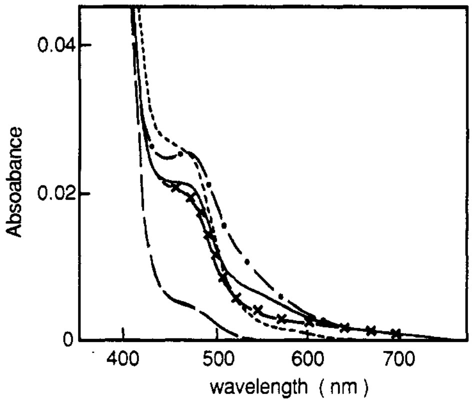


Figure 1. Electronic spectra of viologen derivatives **1** in DMSO ($[V^{2+}]$ = 2.0 mM]): (—) **1a**; (×) **1b**; (- - -) **1c**; (-·-) **1d**; (---) **1e**.

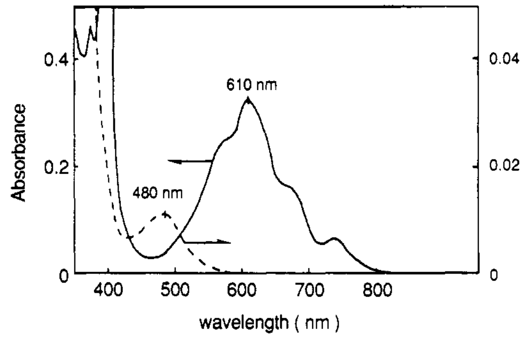


Figure 2. Change of electronic spectra of **1b** in DMSO by photoirradiation with xenon lamp ($\lambda > 350$ nm) ($[V^{2+}]$ = 0.35 mM]): (---) before irradiation; (—) after irradiation.

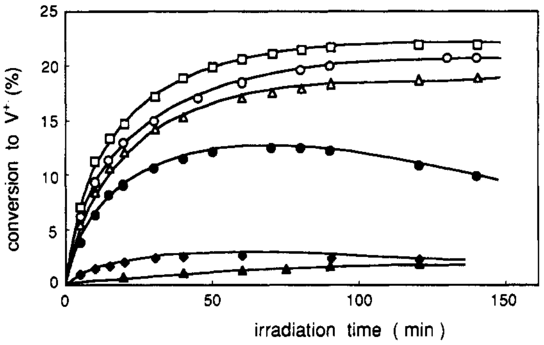
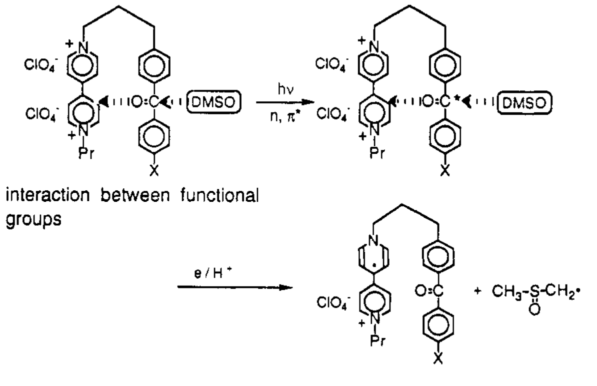


Figure 3. Time dependence of the conversion of **1** to $V^{\bullet+}$ by photoirradiation with xenon lamp ($\lambda > 350$ nm) in DMSO ($[V^{2+}]$ = 0.35 mM]): (△) **1a**; (□) **1b**; (●) **1c**; (○) **1d**; (◆) **1e**; (▲) propyl viologen diperchlorate and benzophenone (1 eq.).

SCHEME I: Proposed Mechanism



The mechanism of the photoreduction of viologen derivatives having the para-substituted benzophenone group in DMSO is proposed in Scheme I. The effective charge donation from the benzophenone group with the electron donating para substituents to the viologen group assisted by DMSO is proposed as observed in its electronic spectrum. By photoirradiation, the carbonyl group is excited and $V^{\bullet+}$ is produced by an electron and proton transfer from DMSO to benzophenone. In the case of **1a** and **1d**, due to the mesomeric effect, and **1b**, due to the mesomeric and inductive effects, the interaction between functional groups was strengthened, and then the benzophenone group is effectively activated to cause electron transfer from DMSO to benzophenone. On the

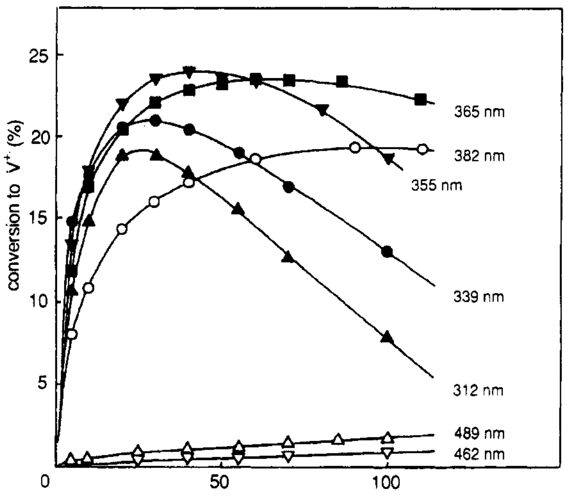


Figure 4. Time dependence of the conversion of **1d** to $V^{\bullet+}$ by monochromatic photoirradiation in DMSO ($[V^{2+}]$ = 0.25 mM]).

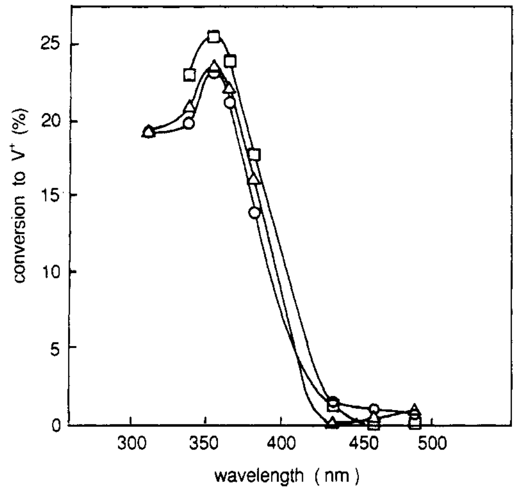


Figure 5. Dependence of the conversion of **1b–1d** to $V^{\bullet+}$ on the wavelength by monochromatic photoirradiation in DMSO ($[V^{2+}]$ = 0.25 mM]): (□) **1b**; (○) **1c**; (△) **1d**.

other hand, the interaction in **1e** was not so strong due to the negative mesomeric and inductive effects of the NO_2 group, then the electron transfer through the benzophenone group might be suppressed.

Conclusion

We could find that the photoreduction of viologen derivatives having various benzophenone groups proceeded unusually by DMSO as a reducing agent. Thus viologen cation radical was produced in an aprotic and neutral media for the first time.

By investigation of the substituent effect on the photoreduction of these viologen derivatives, it has been clarified that the strong intramolecular interaction of viologen and benzophenone groups was important to cause the unusual photoreduction in these systems and these results ascertain the electron relay from DMSO to viologen through the benzophenone group. By developing these results, viologen-mediated photoreaction in aprotic media is in progress.

Experimental Section

Materials. Organic chemicals and solvents used in this study were purified by dehydration with drying agents and distillation.

Typical procedures for the preparation of benzophenone derivatives **4** are as follows. 4-Methoxybenzoyl chloride (**3a**) (7.30 mL, 42.8 mmol) was added dropwise to the suspension of the aluminum chloride (5.70 g, 42.8 mmol) in CH_2Cl_2 (40 mL) at 5 °C. 3-Bromopropylbenzene (**4**) (5.0 mL, 32.9 mmol) was added dropwise to the solution at 10–15 °C. The reaction mixture was refluxed for 10 h and poured into the mixture of concentrated HCl (22 mL) and ice (80 g). The product was extracted with CCl_4. The CCl_4 layer was washed with water and 2% NaOH solution and dried with $MgSO_4$. After filtration and evaporation of the solvent, the residue was dissolved in methanol (50 mL) in order to esterify the excess **3a**. After evaporation of excess methanol, the crude product was chromatographed over silica gel by using a mixture of hexane–ethyl acetate (9:1 v/v) as an eluent to give slightly greenish liquid **4a** (X = MeO) in 79.9% yield. ^{1}H NMR (CCl_4) δ 1.7–2.4 (2 H, m, CH_2), 2.75 (2 H, t, CH_2Ar), 3.30 (2 H, t, $BrCH_2$), 3.73 (3 H, s, OCH_3), and 6.6–8.0 ppm (8 H, m, Ar); IR (neat) 1651 cm^{-1}.

4b (X = Me): brown liquid; yield 48.3%; ^{1}H NMR (CCl_4) δ 1.9–2.5 (5 H, m, CH_2, CH_3), 2.81 (2 H, t, CH_2Ar), 3.33 (2 H, t, $BrCH_2$), and 7.0–7.8 ppm (8 H, m, Ar). **4c** (X = H): brown liquid; yield 46.0%; ^{1}H NMR (CCl_4) δ 1.8–2.4 (2 H, m, CH_2), 2.40 (2 H, t, CH_2Ar), 3.28 (2 H, t, $BrCH_2$), and 6.9–8.2 ppm (9 H, m, Ar). **4d** (X = Cl): light yellow solid; mp 81.0–82.5 °C; yield 85.5%; ^{1}H NMR (CCl_4) δ 1.9–2.5 (2 H, m, CH_2), 2.89 (2 H, t, CH_2Ar), 3.37 (2 H, t, $BrCH_2$), and 7.1–7.9 ppm (8 H, m, Ar). **4e** (X = NO_2): light brown solid; mp 74.0–76.0 °C; yield 78.7%; ^{1}H NMR (CCl_4), δ 1.9–2.5 (2 H, m, CH_2), 2.90 (2 H, t, CH_2Ar), 3.40 (2 H, t, $BrCH_2$), and 7.2–8.4 ppm (8 H, m, Ar).

Typical procedures for the preparation of viologen derivatives (**1**) are as follows. To a solution of 1-propyl-4-(4′-pyridyl)-pyridinium bromide (**2**) (2.00 g, 7.19 mmol) in *N*,*N*-dimethylformamide (DMF) (20 mL) was added **4a** (2.87 g, 8.63 mmol) and the mixture was heated at 100 °C for 24 h. By removal of the solvent under reduced pressure, viologen derivative **1a** was obtained as a bromide salt. The perchlorate salt was obtained by adding aqueous $NaClO_4$ to the methanol solution of the bromide salt. Recrystallization of the product with MeOH gave **1a** (X = MeO) in 27.3% yield. mp 109.5–111.0 °C (decomp); ^{1}H NMR (DMSO-d_6) δ 0.91 (3 H, t, CH_3), 1.7–3.1 (6 H, m, CH_2, CH_2CH_2Ar), 3.86 (3 H, s, OCH_3), 4.4–5.0 (2 H, m, CH_2N^+), 6.9–7.9 (8 H, m, Ar), 8.6–8.9 (4 H, m, pyridinium), and 9.2–9.5 ppm (4 H, m, pyridinium); IR (KBr) 1639 cm^{-1}.

1b (X = Me): Yield 41.0%; mp 206.0–208.0 °C; ^{1}H NMR (DMSO-d_6) δ 0.91 (3 H, t, CH_3), 1.7–3.1 (9 H, m, CH_3CH_2, CH_2CH_2Ar), 4.4–5.1 (4 H, m, CH_2-N^+), 7.2–7.9 (8 H, m, Ar), 8.5–9.0 (4 H, m, pyridinium), and 9.1–9.5 ppm (4 H, m, pyridinium); IR (KBr) 1639 cm^{-1}; Calcd. for $C_{30}H_{33}Cl_2N_2O_9$: C, 56.61; H, 5.23; Cl, 11.87; N, 4.40%. Found: C, 56.60; H, 4.74; Cl, 11.87; N, 4.49%. **1c** (X = H): Yield 64.0%; mp 173–175 °C; ^{1}H NMR (DMSO-d_6) δ 0.94 (3 H, t, CH_3), 1.6–3.1 (6 H, m, CH_2, CH_2CH_2Ar), 4.4–5.0 (4 H, m, CH_2-N^+), 7.2–7.8 (9 H, m, Ar), 8.5–8.8 (4 H, m, pyridinium), and 9.1–9.3 ppm (4 H, m, pyridinium); Calcd. for $C_{29}H_{30}Cl_2N_2O_9$: C, 56.05; H, 4.87; Cl, 11.41; N, 4.51%. Found: C, 55.90; H, 4.94; Cl, 11.48; N, 4.51%. **1d** (X = Cl): Yield 61.5%; mp 155.0–158.0 °C (decomp); ^{1}H NMR (DMSO-d_6) δ 0.94 (3 H, t, CH_3), 1.7–3.1 (6 H, m, CH_3, CH_2CH_2Ar), 4.4–5.0 (4 H, m, CH_2N^+) 7.1–7.9 (8 H, m, Ar), 8.5–9.0 (4 H, m, pyridinium), and 9.1–9.5 ppm (4 H, m, pyridinium). **1e** (X = NO_2): Yield 85.6%; mp 211.0–215.0 °C (decomp); ^{1}H NMR (DMSO-d_6) δ 0.94 (3 H, t, CH_3), 1.7–3.1 (6 H, m, CH_2, CH_2H_2Ar), 4.3–5.0 (4 H, m, CH_2-N^+), 7.3–8.5 (8 H, m, Ar), 8.5–9.0 (4 H, m, pyridinium), and 9.2–9.5 ppm (4 H, m, pyridinium); Calcd. for $C_{29}H_{29}Cl_2N_3O_{11}$: C, 52.26; H, 4.39; Cl, 10.64; N, 6.30%. Found: C, 51.71; H, 4.32; Cl, 10.82; N, 6.20%.

Apparatus and Procedures. The DMSO solution of viologen derivative **1** was put into a 10 × 10 mm quartz cell equipped with a three-way stopcock and bubbled with argon gas for 30 min and the cell was quickly sealed. The solution was photoirradiated by a 500-W xenon lamp (USIO UXL 500D) at a distance of 10 cm away from the cell. UV 35 and HA 50 filters were set to cut off the light of less than 350 nm and thermal rays. The photoreaction was monitored by the measurement of electronic spectra of the solution at various intervals by Shimadzu UV-2100 spectrometer.

For monochromatic irradiation, JASCO CRM-FA Spectro Irradiator equipped with a xenon lamp (2.0 kW) was used. The relative light intensities of monochromatic lights were counted to be 0.46 (312 nm), 1.00 (339 nm, 8.5 mW/cm^2), 1.06 (355 nm), 1.08 (365 nm), 1.07 (382 nm), 1.52 (435 nm), 1.59 (462 nm), and 1.48 (489 nm).

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Luminescence Dynamics and ^{13}C NMR Characteristics of Dinuclear Complexes Exhibiting Coupled Lanthanide(III) Cation Pairs

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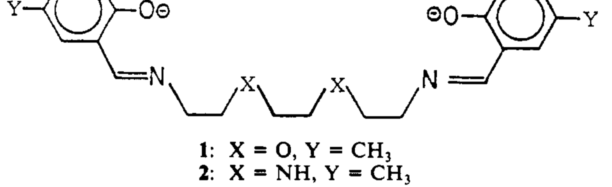
Luminescence and cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR properties of lanthanide dinuclear macrocyclic complexes of a compartmental Schiff base chelate (**1**) derived from the condensation of 2,6-diformyl-*p*-cresol and 3,6-dioxa-1,8-octanediamine are reported. The Schiff base chromophore in **1** is a strong light absorber and an efficient sensitizer for intense $Tb^{3+}(^5D_4)$ and $Eu^{3+}(^5D_0)$ ($T < 110$ K) emission which does not exhibit self-quenching effects. Emission from Tb^{3+} is sensitized by the ligand singlet state; in striking contrast, Eu^{3+} emission is sensitized by the triplet state and reveals an unusual nonradiative quenching process at $T > 110$ K with a thermal barrier of ≈ 2300 cm^{-1}. Weak emission is observed from $Dy^{3+}(^4F_{9/2})$, $Sm^{3+}(^4G_{5/2})$, and $Pr^{3+}(^1D_2)$ diluted in Gd^{3+} (i.e., from Gd^{3+}–Ln^{3+} heteropairs, Ln = Pr, Sm, Dy). Intramolecular metal–metal (Ln–Ln = 4 Å) interactions account for the greatly quenched emission from Sm^{3+}–Sm^{3+} and Dy^{3+}–Dy^{3+} homopairs compared to Gd^{3+}–Ln^{3+} heteropairs (Ln = Sm, Dy). Gd^{3+}–Ln^{3+} emission lifetimes at 77 K are 1610 (Tb^{3+}), 890 (Eu^{3+}), 14 (Dy^{3+}) and ≈ 13 μs (Sm^{3+}). Nonradiative relaxation processes at 77 K in dilute Ln^{3+}:$Gd_2\mathbf{1}(NO_3)_4 \cdot H_2O$, being temperature independent for Sm^{3+} and Eu^{3+} but temperature dependent for Tb^{3+}, follow the energy gap law with $\alpha \approx -10^{-3}$ cm and $B \approx 2 \times 10^8$ s^{-1}. CP-MAS data show paramagnetic broadening of ^{13}C resonances which increases with the magnetic moment of Ln^{3+}. Surprisingly, no significant shifts in resonance positions corresponding to the changing nature of paramagnetic Ln^{3+} ions are observed.

Introduction

Spectroscopic properties of lanthanide(III) (Ln^{3+}) complexes in which the Ln^{3+} cations are tightly locked in coordination cavities of organic chelates have been extensively studied.[1-22] When bound to organic chelates bearing chromophoric sites which exhibit large extinction coefficients, Eu^{3+} and Tb^{3+} cations are normally good luminophores[23,24] at room temperature with potential applications in biomedical diagnostics.[25] In this case, population of the luminescent $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states is achieved by efficient energy-transfer processes involving the organic chromophores as exciton donors.[9,12-19,23-28]

We have been interested in the preparation, structure, and spectroscopy of dinuclear lanthanide complexes in which a pair of Ln^{3+} cations is tighly locked into the coordination cavities of a single chelate.[5,6,29] With suitable chromophores, dinuclear complexes, like mononuclear ones, could exhibit desirable light-gathering (antenna effect)[23-28] and exciton-transfer characteristics. But because of the proximity of the Ln^{3+} ions constituting the Ln^{3+}–Ln^{3+} homopair or $Ln(1)^{3+}$–$Ln(2)^{3+}$ heteropair trapped by the dinucleating chelate, f–f electronic coupling might enable control of luminescence decay kinetics, exciton transfer, and migration processes as well as electron spin relaxation characteristics. Such an achievement could open possibilities for novel tunable luminescent and paramagnetic probes.

We have prepared and structurally characterized dinuclear complexes of **1**[5]. The Schiff base chromophore in these complexes



1: X = O, Y = CH_3
2: X = NH, Y = CH_3
3: X = O, Y = Cl