

# Notes

## Temperature-Dependent Redox Chemistry of $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ in Nonaqueous Media

Hyun Lee, Ok-Sang Jung<sup>†</sup>, and Seungwon Jeon\*

Department of Chemistry, Chonnam National University, Kwang-ju 500-757, Korea

<sup>†</sup>Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

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The electron-transfer chemistry of transition metal complexes in nonaqueous media has been of continuing major interest. The semiquinonate (SQ) and catecholate (Cat) ligands have partially filled and filled molecular orbitals that are close in energy to transition metal d orbitals.<sup>1</sup> The complexes of cobalt ion and quinone ligand containing nitrogen-donor coligand showed facile intramolecular charge transfer between cobalt and quinone ligand in toluene solution and in the solid state (1).<sup>2-10</sup>



$\text{Co}^{\text{II}}$  complex predominates in toluene solution at higher temperature, and  $\text{Co}^{\text{III}}$  complex is stabilized with the decrease of solution temperature. Isomerism of the complex is related by the electron transfer between core metal and quinone ligand. Temperature or photo driven equilibria between the isomers has been observed for the complexes of cobalt ion and quinone ligands. Equilibria between valence isomers occur in separate electron transfer and spin transition steps.<sup>5,8</sup>

Electrochemistry of quinones and metal complexes coordinating with quinone ligands has been investigated in nonaqueous solvents.<sup>11-15</sup> The electron transfer for metal-quinone complexes involves the ligand rather than the metal, and the redox processes of quinone ligands are very important for the understanding of their electrochemistry. Electrochemistry of iron complexes with quinone ligands containing nitrogen donor coligand is recently reported, but is less understood in nonaqueous solvents.<sup>16,17</sup>

Recently it was reported that an unexpectedly large change in oxidation state is dependent on the remote group X of  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  [phen; phenanthroline] along with temperature dependence in toluene.<sup>18</sup> In the present study, we describe the temperature-dependent redox chemistry of  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  containing 4,7-disubstituted phenanthroline as nitrogen-donor coligands and the solvent-dependent transition temperature of them in nonaqueous solvents.

### Experimental

**Material.**  $X_2\text{-phen}$  (X=H, ph) and Dicobaltoctacarbonyl were purchased from Strem and Aldrich, respectively.  $\text{Cl}_2\text{-phen}$  ligand,<sup>19</sup> 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ),<sup>20</sup> and  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  (X=H, ph, Cl)<sup>18</sup>

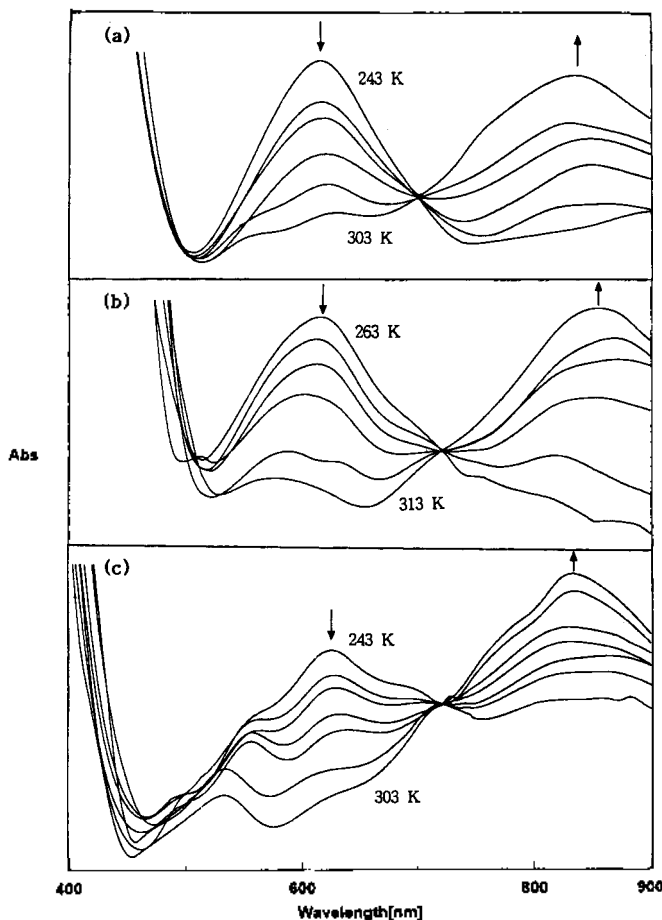
were prepared using literature procedure. Anhydrous acetonitrile (MeCN), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), toluene, and dimethyl formamide (DMF) were used as received from Aldrich. Tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) was used as a supporting electrolyte.

**Instrumentation and Methodology.** The voltammetric measurements were accomplished with a three electrode potentiostat (Bioanalytical Systems [BAS], Model CV-27) and a Rikadenki Model RW 21T recorder. A platinum-wire electrode separated from the analyte compartment by a medium porosity glass frit was used as an auxiliary electrode. An Ag/AgCl electrode supplied by BAS was used as a reference electrode, and the potential is approximately -45 mV relative to a saturated calomel electrode (SCE). A 3.0 mm diameter glassy carbon and 1.6 mm diameter platinum were employed as working electrodes for the redox reactions of cobalt-quinone complexes. All working electrode surfaces were highly polished with alumina paste prior to each experiment. Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell containing a Pt mesh working electrode via controlled potential electrolysis using CV-27 potentiostat with the three electrode system. Absorption spectra were recorded on a Jasco V-530 spectrophotometer equipped with a HMC-358 constant temperature cell holder. Infrared spectra were obtained in 5000-400  $\text{cm}^{-1}$  range on a Perkin Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets. All experiments are carried out under anaerobic conditions.

### Results and Discussion

#### Electronic Spectra of $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ .

Since  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{II}}$  complexes have characteristic electronic spectra, absorption spectroscopy has been used to monitor equilibria in different solvents over an appropriate temperature range. It has been known that the complexes of  $\text{Co}^{\text{III}}(\text{N-N})(\text{SQ})(\text{Cat})$  show characteristic absorptions in the 600-650 nm range of the visible region, and  $\text{Co}^{\text{II}}(\text{N-N})(\text{SQ})_2$  complexes give characteristic absorptions in the 800-850 nm range. The temperature-dependent spectra for  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  are shown in Figure 1 in several solvents. It is well known that  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  is stable in toluene solution, but is now unclear about their stability in non-aqueous solvents which can be used for electrochemistry of transition metal complexes.  $\text{Co}^{\text{III}}$  form is generally



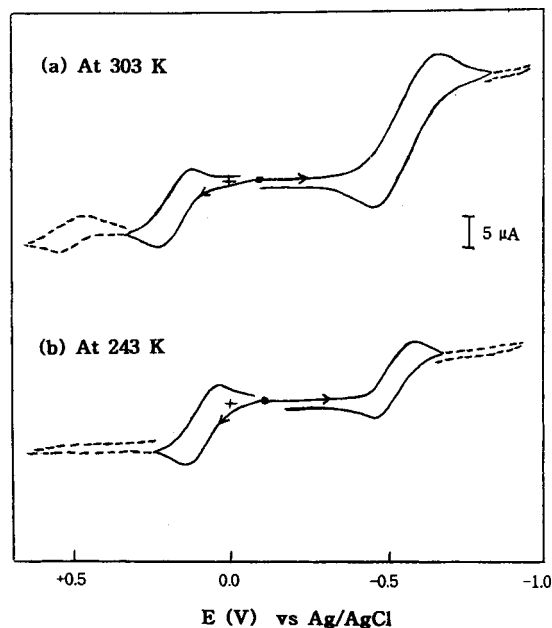
**Figure 1.** The temperature-dependent spectra for 0.15 mM  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  in (a) methylene chloride (243 K, 253 K, 263 K, 273 K, 293 K, 303 K), (b) acetonitrile (263 K, 273 K, 283 K, 293 K, 303 K, 313 K), and (c) toluene (243 K, 253 K, 263 K, 273 K, 283 K, 293 K, 303 K).

decreased with the increase of solution temperature, and  $\text{Co}^{\text{II}}$  form is increased concomitantly.  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  predominantly exists as  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-DBSQ})(3,6\text{-DBCat})$  at lower temperature, whereas as  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-DBSQ})_2$  at higher temperature. The  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  transition temperature ( $T_c$ ) is defined as the approximate temperature at which concentrations of  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{II}}$  forms of the cobalt complexes are equal in solution. The  $T_c$  of  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  determined from systematic experiments with solution temperature may be about 263 K in toluene solution (approximately 283 K in  $\text{CH}_2\text{Cl}_2$ , 293 K in MeCN). IR spectral characterization on  $\text{Co}^{\text{III}}$  complexes shows that an intense transition in the  $4000\text{ cm}^{-1}$  region of the infrared appears characteristically for complexes of this charge distribution.<sup>18</sup> This band is assigned as the charge transfer transition from Cat ligand to cobalt that is associated with the electron transfer step. In the previous paper,<sup>18</sup> the band intensity is dependent on the remote functional group ( $X=\text{Me}$ , H, Ph, and Cl) of  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ . The band intensity is linearly correlated with Hammett constants of X group of the coligands. According to IR and visible spectra,  $(\text{Cl}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-DBSQ})_2$  is predominant in the solid state and its  $T_c$  seems to be about 235 K

in toluene solution (approximately 245 K in  $\text{CH}_2\text{Cl}_2$ , 260 K in MeCN), but  $(\text{phen})\text{Co}^{\text{III}}(3,6\text{-DBSQ})(3,6\text{-DBCat})$  is major in the solid state and  $T_c$  of about 245 K in toluene (about 250 K in  $\text{CH}_2\text{Cl}_2$ , 260 K in MeCN). In this study, systematic experiments for  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  confirm that the order of transition temperature ( $T_c$ ) between tautomers in solvents is apparently toluene <  $\text{CH}_2\text{Cl}_2$  < MeCN, which may be ascribed to the donation effect of solvents. It is also observed that  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  is stable in  $\text{CH}_2\text{Cl}_2$  or MeCN as well as toluene solution at the temperature lower than  $T_c$ . However,  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  is decomposed in DMF, and can not be determined their  $T_c$ .

**Electrochemistry of  $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ .** It is well known that benzoquinone (BQ) reduces electrochemically to semiquinone anion-radical (SQ), and then reduces catecholate dianion (Cat). An initial negative scan for 3,6-DBBQ yields two stepwise redox couples at  $-0.56\text{ V}$  vs Ag/AgCl and  $-1.15\text{ V}$  in  $\text{CH}_2\text{Cl}_2$  at 293 K (scan rate:  $50\text{ mV/sec}$ ), and they are quasi-reversible processes.  $X_2\text{-phen}$  used as a coligand of cobalt-quinone complexes doesn't show any redox peaks within potential window employed.

Figure 2 illustrates the temperature-dependent cyclic voltammograms (CVs) for  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  in  $\text{CH}_2\text{Cl}_2$  containing  $0.1\text{ M Bu}_4\text{NClO}_4$ . According to Figure 2a at higher temperature (303 K), an initial positive scan for  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  yields two reversible redox couples at  $+0.16\text{ V}$  and  $+0.50\text{ V}$ . Cyclic voltammograms for the first oxidation of the  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  are obtained at various scan rates, and the dependence of the anodic current as a function of the square root of the scan rate is linear as expected from a diffusion-controlled process. The anodic peak current at a constant scan rate is linearly proportional to the concentration of the cobalt complex. Because the

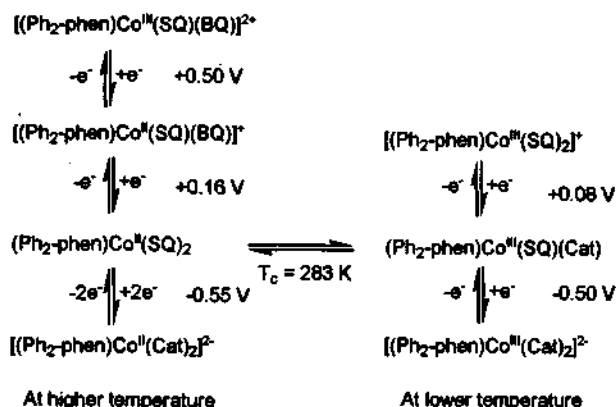


**Figure 2.** The temperature-dependent cyclic voltammograms (CVs) for  $3.0\text{ mM } (\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  in  $\text{CH}_2\text{Cl}_2$  containing  $0.1\text{ M Bu}_4\text{NClO}_4$  at Pt electrode, (a) at 303 K and (b) at 243 K.

peak separation between first oxidation and its corresponding reduction peak is about 90 mV, its electrode reaction is quasi-reversible (about 60 mV in the case of reversible process if the number of electron transferred is 1). Spectroscopic results show that  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  exists as  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  at 303 K. The presence of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  at higher temperature was confirmed by IR and magnetic measurements as well as electronic spectra.<sup>18</sup>  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  can oxidize to  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})(3,6\text{-BQ})]^+$  by ligand centered or  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})_2]^+$  by cobalt centered. Optically transparent thin-layer controlled potential coulometry at +0.30 V gives the invariance of Soret band and an appearance of new band at 410 nm which can be obtained from free benzoquinone. The invariance of Soret band is an evidence of the invariance of cobalt oxidation state. These results suggest that the first oxidation of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  produces  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})(3,6\text{-BQ})]^+$  by ligand centered, and then  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})(3,6\text{-BQ})]^+$  slowly decomposes to free BQ and  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})]^+$ . The second oxidation current is smaller than first one, and this result may be responsible for slow charge transfer for the oxidation of  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})(3,6\text{-BQ})]^+$  to  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-BQ})]^{2+}$  by cobalt centered. On the basis of the spectroscopic result,  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  converts to  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-Cat})$  by intramolecular electron transfer with the decrease of solution temperature.

According to Figure 2b at lower temperature (243 K), likewise an initial positive scan for  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-Cat})$  yields apparently one reversible redox couple at +0.08 V. This oxidation potential (+0.08 V) of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-Cat})$  is slightly shift to negative direction compared to that (+0.16 V) of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  at higher temperature. Thin-layer controlled potential coulometry at +0.15 V gives the invariance of Soret band. The invariance of Soret band is an evidence of the invariance of cobalt oxidation state. These result suggests that the first oxidation of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-Cat})$  produces  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})_2]^+$  by ligand centered. The peak current of first oxidation at lower temperature is close to that at higher temperature. The second oxidation peak is not shown here.

An initial negative scan yields one redox couple as shown in Figure 2. The first reduction half-wave potential is dependent upon the solution temperature ( $-0.55$  V for  $E_{pc} = -0.63$  V and  $E_{pa} = -0.46$  V at 303 K,  $-0.50$  V for  $E_{pc} = -0.55$  V and  $E_{pa} = -0.46$  V at 243 K). The peak separation between reduction and its corresponding oxidation peak is about 170 mV at higher temperature and 90 mV at lower temperature. On the basis of half-wave potential and peak separation, at higher temperature the reduction involves closely step-by-step two reduction processes, but at lower temperature the reduction involves one electron process. The comparison of the current ratio of the first reduction and the first oxidation peak will give an information about the number of electron transferred. The ratio of peak current (first reduction/first oxidation current) is close to 1 at 243 K whereas about 2 at 303 K. This result confirms that the reduction of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  is apparently two-electron process at higher temperature, and the reduction of  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-Cat})$  is one-electron process at



Scheme 1.

lower temperature. Thin-layer controlled potential coulometry at  $-0.65$  V gives the invariance of Soret band. The invariance of Soret band is an evidence of the invariance of cobalt oxidation state. Overall results suggest that  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-SQ})_2$  reduces closely step-by-step to  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-Cat})_2]^{2-}$  by two-electron transfer at higher temperature, whereas  $(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-SQ})(3,6\text{-Cat})$  reduces  $[(\text{Ph}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-Cat})_2]^{2-}$  by one-electron transfer at lower temperature. At temperature close to  $T_c$ , their redox chemistry is mixed by two tautomers. In summary temperature-dependent redox chemistry for  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  in  $\text{CH}_2\text{Cl}_2$  is outlined in Scheme 1.

The temperature-dependent CVs for  $(\text{Cl}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  and  $(\text{phen})\text{Co}(3,6\text{-DBBQ})_2$  in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{Bu}_4\text{NClO}_4$  are similar to those for  $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ . Because the difference between them is transition temperature, their redox chemistry depends on the solution temperature. The redox chemistry of  $(\text{X}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  containing 4,7-disubstituted phenanthroline as nitrogen-donor coligands depends on the solution temperature and is mainly quinone-ligand centered rather than metal centered in  $\text{CH}_2\text{Cl}_2$ . The  $T_c$  of  $(\text{X}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$  is dependent upon the solvent employed.

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## Energy Transfer from $Gd^{3+}$ to $Eu^{3+}$ in $(Y, Gd)BO_3:Eu^{3+}$

Yong Yune Shin, Youngrag Do<sup>†</sup>, and Youhyuk Kim\*

*Department of Chemistry and Information Display Research Center, Dankook University, Cheonan, Choongnam 330-714, Korea*

<sup>†</sup>*Samsung Display Device Co. Ltd. 575 Shin-Dong, Paldal-Gu, Suwon, Kyungki-Do 442-390, Korea*

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Phosphors comprising rare-earth borate activated by rare earth ions have been neglected in the past, partly because of their lack of applicability to the field of display panels. Recently, however, some phosphors based on rare-earth borate have been used in color plasma display panel (PDP) which is the most promising flat display for the large area display.<sup>1</sup> Phosphors used in PDP are excited with vacuum ultraviolet radiation (147, 172 nm) from a Penning mixtures (Ne+Xe) in the panel. Naturally the phosphors are required to have a good quantum efficiency in the region below 200 nm. In this context rare-earth borates which give intense absorption peaks in this region have been selected as suitable host materials in PDP phosphors.<sup>2</sup> One of efficient red phosphors in PDP is a  $(Y, Gd)BO_3:Eu$ , which contains two components in the host lattice.

Based on previously investigated metal oxide systems, which show an energy transfer from pair Gd ions to other  $RE^{3+}$ ,<sup>3</sup> gadolinium ions in the  $(Y, Gd)BO_3:Eu^{3+}$  are expected to transfer an absorbed energy to  $Eu^{3+}$ . We have investigated luminescence properties of  $(Y, Gd)BO_3:Eu$  as a function of  $Eu^{3+}$  and  $Gd^{3+}$  to elucidate the role of gadolinium ions in this phosphor.

### Experimental

Phosphors with the general formula  $[(Y_{0.9-x}, Gd_{0.1+x})_{1-x}Eu_x]BO_3$  ( $x=0.01-0.2$ ),  $[(Y_{0.9}, Eu_{0.1})_{1-x}Gd_x]BO_3$  ( $x=0.01-0.7$ ) and  $(Y_{0.9-x}, Gd_x)BO_3:Eu_{0.1}$  ( $x=0-0.9$ ) were prepared by the usual solid-state reaction.<sup>4</sup> The exact compositions of the phosphors are described in the text whenever such descriptions are necessary. The properties of phosphors are generalized

and do not pertain to one specific phosphor composition.

The raw materials  $Y_2O_3$ ,  $Gd_2O_3$ ,  $Eu_2O_3$  and  $H_3BO_3$  were thoroughly mixed with a small amount of a flux. The mixture was then charged in an alumina crucible with an alumina lid and fired at 1100 °C for 2h. Of the raw materials,  $Y_2O_3$  (Molycorp) and  $Eu_2O_3$  (Molycorp) were at 99.99% purity and  $Gd_2O_3$  (ShinEtsu) was 99.9% purity. The other raw materials were of reagent grade.

The phosphors were characterized by X-ray diffraction analysis. The excitation spectra between 200 and 400 nm were obtained with a Filter OG530 on excitation slit 0.28 mm and emission slit 0.9 mm by a home-made spectrofluorimeter (monochromator:ORIEL, light source:ORIEL 150W, detector:HAMAMATUS R-928) at KIST in Seoul. The emission spectra between 400 and 700 nm were obtained with a 254 nm excitation wavelength by a Samsung optical spectra multichannel analyzer (OSMA). For selective irradiation, the emission spectra were collected by a home-made spectrofluorimeter at Samsung Co. in Suwon as a function of excitation wavelength.

### Results and Discussion

Prepared powders of  $(Y, Gd)BO_3:Eu^{3+}$  show a single phase which corresponds to a solid solution on all the powder patterns. This is expected by a similarity of the crystal ionic radii of  $Y^{3+}$  (0.93Å),  $Gd^{3+}$  (0.94Å) and  $Eu^{3+}$  (0.95Å).<sup>5</sup> The replacement of  $Y^{3+}$  ions with  $Gd^{3+}$  and  $Eu^{3+}$  ions is, therefore, easily occurred to give a solid solution.

**Excitation Spectra.** Figure 1 shows the excitation spectra of various compositions of  $(Y_{0.9-x}, Gd_x)BO_3:Eu_{0.1}$  ranging from 200 to 425 nm with the emission line at 593 nm. The concentration of activator,  $Eu^{3+}$  maintains a con-

\*To whom all correspondence should be addressed.