Circularly dichroism and circularly polarized luminescence induction behaviors of a Tb-cyclen complex supported on silica with chiral phenylethylamine ligands

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We investigated the preparation of new chiral molecular structures on $\mathrm{SiO_2}$ surface by the attachment of a racemic and luminous Tb complex ($^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$) on a $\mathrm{SiO_2}$ surface modified with chiral phenylethylamine ligands (**(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$**), and the equilibrium of dynamic chirality of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ was successfully shifted on the $\mathrm{SiO_2}$ surface. In this presentation, we discuss the interpretation about the major helical conformation of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ on **(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$**, by taking the possible helical conformation of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ with chiral phenylethylamine ligands (**(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$**) in solution system into account.

$^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$**/(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** were prepared by the attachment of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ on **(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** (**Figure 1**), respectively. Not only solid-state circularly polarized luminescence (CPL) derived from f-f emissions of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ but also solid-state circular dichroism (CD) were observed on $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$**/(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$**. The solid-state CD spectra of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$**/(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** showed mirror-imaged peaks in the range of 280-360 nm (**Figure 2**), suggesting the equilibrium shift of dynamic chirality of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ on **(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** in the ground state. The origin of CD was estimated to be derived from π-π^* transition of biphenyl moiety of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ coordinated with **(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$**, as calculated by DFT, and the comparison of the simulated CD spectra and experimental ones suggested that the major helical conformation of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ on **(*R*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** would be in Δ form and that of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$ on **(*S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** would be in Λ form, respectively (**Figure 1**).

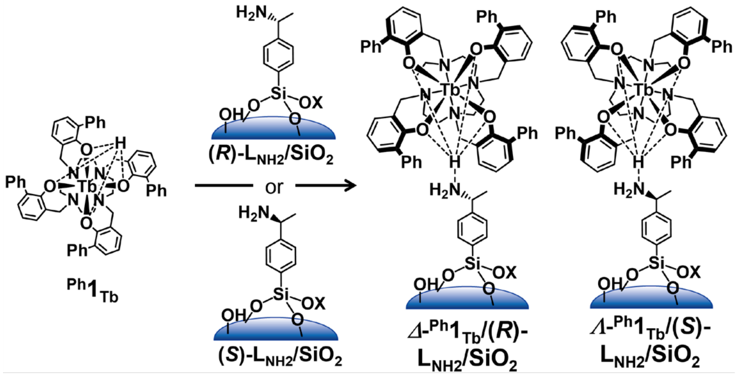

Figure 1. Preparation scheme of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$**/(*R* or *S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** and their possible major helical conformations.

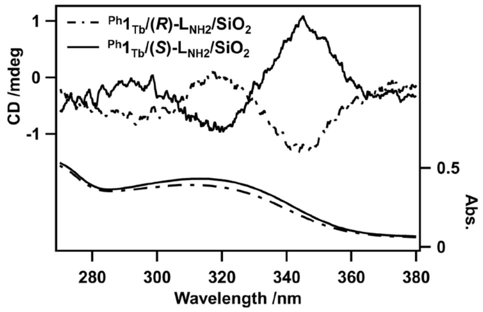

Figure 2. Solid-state CD spectra and absorption spectra (in nujol) of $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$**/(*R*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** (dashed line) and $^{\mathrm{Ph}}\mathbf{1}_{\mathbf{Tb}}$**/(*S*)-$\mathbf{L}_{\mathbf{NH2}}$/$\mathbf{SiO_2}$** (solid line).