

Surface Attachment and Circularly Polarized Luminescence of Luminous Terbium Complex on Silica Surface with Chiral Ligands

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Chiral metal complexes immobilized on solid surfaces are investigated for applications to solid chiral sensors, heterogeneous asymmetric catalysts etc. We investigated a new preparation method of surface-attached chiral metal complexes via chirality induction of metal complexes on a solid surface modified with chiral ligands. The induction of the chirality of an achiral terbium (Tb) complex ($\mathbf{1}_{\text{Tb}}$)¹ was investigated on a silica (SiO_2) modified with chiral benzyl alcohol ligands (Figure 1).

SiO_2 surface was modified with newly-prepared chiral benzyl alcohol ligands ($\mathbf{L(R/S)}$) and SiO_2 attaching the chiral ligands ($\mathbf{L(R/S)/SiO}_2$) was prepared. UV-vis and FT-IR suggested that the structure of $\mathbf{L(R/S)}$ was maintained on the SiO_2 surface. The solid-state CD of $\mathbf{L(R/S)/SiO}_2$ showed inverted peaks at 230 nm (Figure 2(A)), which was similar to the solution-state CD of $\mathbf{L(R/S)}$, suggesting that the chirality of $\mathbf{L(R/S)}$ was retained on the SiO_2 surface.

$\mathbf{1}_{\text{Tb}}$ was attached to $\mathbf{L(R/S)/SiO}_2$ by the impregnation method ($\mathbf{1}_{\text{Tb/L(R/S)/SiO}_2}$). The DR UV-vis of $\mathbf{1}_{\text{Tb/L(R/S)/SiO}_2}$ showed absorption peak at around 301 nm (Figure 2(B)), which was similar to the solution-state UV-vis of $\mathbf{1}_{\text{Tb}}$, suggesting that the structure of $\mathbf{1}_{\text{Tb}}$ was kept on the SiO_2 surface. The solid-state CPL of $\mathbf{1}_{\text{Tb/L(R/S)/SiO}_2}$ showed inverted CPL peaks around 550 nm, which suggested that the chirality of $\mathbf{1}_{\text{Tb}}$ was actually induced by the coordination of $\mathbf{1}_{\text{Tb}}$ to $\mathbf{L(R/S)/SiO}_2$. The CPL peak intensities of $\mathbf{1}_{\text{Tb/L(R/S)/SiO}_2}$ were obviously larger than that of $\mathbf{1}_{\text{Tb/L(R/S)-1-phenylethanol}$ in acetonitrile solution. These results strongly indicated that the unique CPL property of $\mathbf{1}_{\text{Tb}}$ was induced at the SiO_2 surface by the coordination to the surface-functionalized chiral ligands.

1) H. Nakai, *et al.*, *Chem. Commun.*, **2014**, 50, 15737-15739.

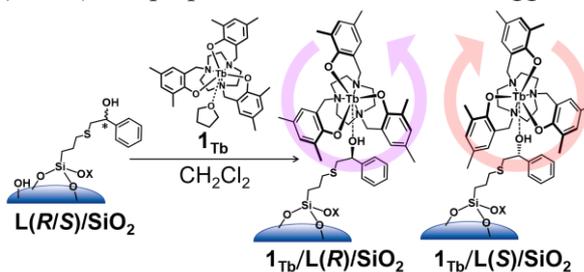


Figure 1. Chirality induction of $\mathbf{1}_{\text{Tb}}$ with $\mathbf{L(R/S)/SiO}_2$.

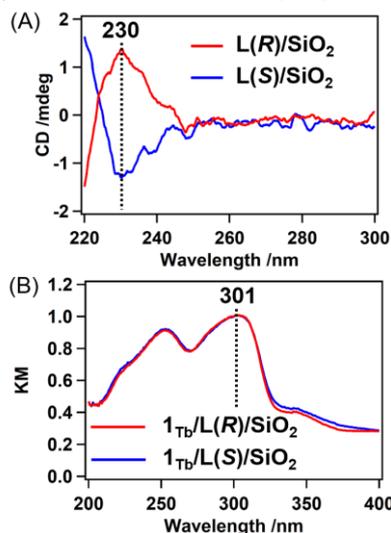


Figure 2. (A) Solid-state CD spectra of $\mathbf{L(R/S)/SiO}_2$. (B) DR UV-vis spectra of $\mathbf{1}_{\text{Tb/L(R/S)/SiO}_2}$.