Immobilization of Terbium Complex on Solid Surface with Chiral Moiety

([1]*Grad. Sch. Sci., Nagoya Univ.*, [2]*Grad. Sch. Sci. Eng., Kindai Univ.* [3]*RCMS, Nagoya Univ.*)
○Sora Shirai,[1] Satoshi Muratsugu,[1] Hidetaka Nakai,[2] Mizuki Tada[1,3]

Keywords: Terbium Complex; Chirality; Immobilization; Surface; Circularly Polarized Luminescence

Chiral metal complexes immobilized on solid surfaces are promising for chiral materials such as solid chiral sensors and heterogeneous asymmetric catalysts. The preparation of a new chiral coordination structure on silica solid surface was investigated by the chirality induction of an achiral metal complex and a solid surface modified with chiral moieties. In this study, we report the efficient chirality induction of an achiral Tb complex ($^{R}\mathbf{1}_{Tb}$) on a SiO_2 surface modified with chiral ligands (denoted as **L(*R*/*S*)/SiO$_2$**, Figure 1).

A Tb complex with a bulky ligand connecting *t*-butyl groups ($^{t\text{-Bu}}\mathbf{1}_{Tb}$) was used for the attachment of chirality-modified silica surface (Figure 1). A triazacyclononane-based tris-phenol with *t*-butyl group ($^{t\text{-BuMe}}$**ArOH)$_3$tacn**) was newly synthesized and characterized by ^{1}H NMR and ESI-MS. ($^{t\text{-BuMe}}$**ArOH)$_3$tacn** was reacted with $Tb(OTf)_3$ under basic conditions in DMF, and the UV-vis absorption spectra of the obtained crude product showed the significant shift of the peak attributed to π- π* transition from 286 nm to 299 nm (Figure 2), suggesting the formation of $^{t\text{-Bu}}\mathbf{1}_{Tb}$. A chiral ligand with a rigid phenylene linker structure was synthesized and attached on a silica surface and $^{R}\mathbf{1}_{Tb}$ was immobilized on the silica surface as shown in Figure 1. The effect of a rigid linker structure of the surface-attached chiral ligands and the bulky ligand of the Tb complex on the chirality induction on the SiO_2 surface by the immobilization of $^{R}\mathbf{1}_{Tb}$ onto **L(*R*/*S*)/SiO$_2$** will be presented.

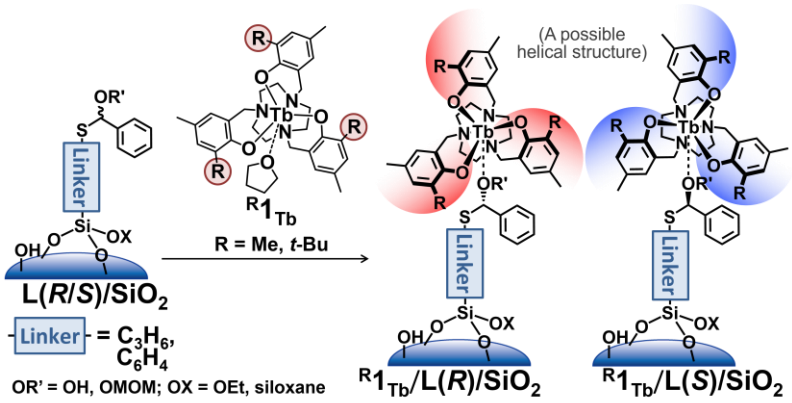

Figure 1. The preparation scheme of $^{R}\mathbf{1}_{Tb}$ on **L(*R*/*S*)/SiO$_2$**.

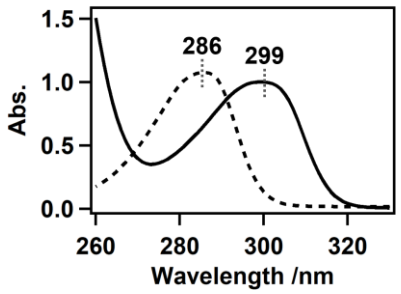

Figure 2. Solution-state UV-vis spectra of ($^{t\text{-BuMe}}$**ArOH)$_3$tacn** (dashed line, 1.3×10^{-4} M in CH_2Cl_2) and that reacted with $Tb(OTf)_3$ (solid line, 0.20 mg/mL in CH_2Cl_2).