Chirality Induction of Luminous Tb Complexes on Silica Surface Functionalized with Chiral Benzylamine Ligands

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Immobilization of chiral metal complexes on solid surfaces produces chiral metal complexes on solid materials, which are applied to chiral sensors and heterogeneous asymmetric catalysts etc. The preparation of new chiral molecular structures on SiO_2 surface was investigated by the attachment of an achiral Tb complex on a SiO_2 surface modified with chiral moieties and the chirality induction of an achiral Tb complex ($^{Ph}\mathbf{1}_{Tb}$) on a SiO_2 surface with chiral benzylamine ligands ($\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$) was successfully achieved.

A chiral ligand ($\mathbf{L_{NHBoc}}(\boldsymbol{R}/\boldsymbol{S})$), whose amine moiety was protected with a *t*-butoxycarbonyl (Boc) group, was newly synthesized and characterized by ^{1}H NMR, FT-IR, and ESI-MS. $\mathbf{L_{NHBoc}}(\boldsymbol{R}/\boldsymbol{S})$ was attached to a SiO_2 surface, and the Boc group was finally deprotected to prepare $\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$ (Figure 1). Solid-state CD spectra of $\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$ showed inverted CD peaks derived from the surface-attached chiral benzylamine moieties, suggesting the formation of a homo-chiral SiO_2 surface with chiral benzylamine.

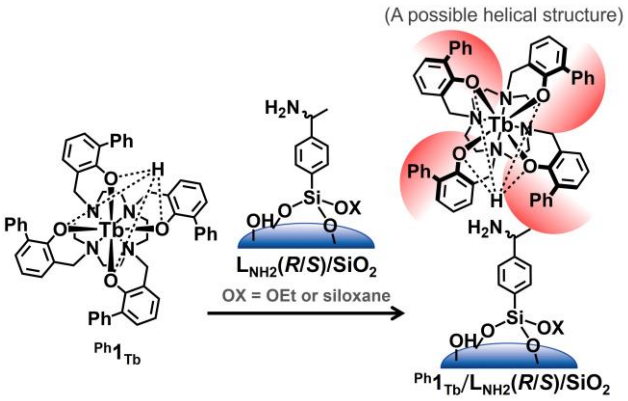

Figure 1. Preparation of $^{Ph}\mathbf{1}_{Tb}/\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$.

An achiral Tb complex with a tetraazacyclododecane-based tetrakis-(2-phenyl-phenoxide) ligand ($^{Ph}\mathbf{1}_{Tb}$) was immobilized on $\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$ (Figure 1). Tb L_{III}-edge EXAFS of $^{Ph}\mathbf{1}_{Tb}/\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$ were similar to that of $^{Ph}\mathbf{1}_{Tb}$, indicating that the coordination structure of the precursor $^{Ph}\mathbf{1}_{Tb}$ was maintained on the SiO_2 surface (Figure 2). Solid-state CPL spectra of $^{Ph}\mathbf{1}_{Tb}/\mathbf{L_{NH2}}(\boldsymbol{R}/\boldsymbol{S})/\mathbf{SiO_2}$ showed inverted CPL peaks derived from f-f emissions of $^{Ph}\mathbf{1}_{Tb}$, strongly suggesting that the chirality of $^{Ph}\mathbf{1}_{Tb}$ was successfully induced on the attached SiO_2 surface with the chiral benzylamine ligands.

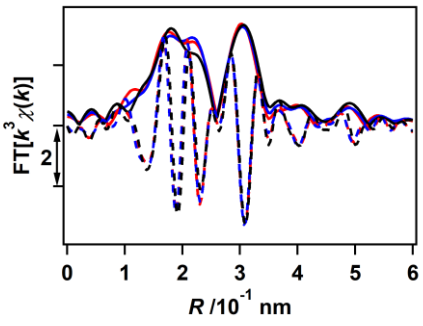

Figure 2. k^3-weighted Tb L_{III}-edge EXAFS Fourier transforms (k = 30 — 105 nm^{-1}) of $^{Ph}\mathbf{1}_{Tb}$ (black), $^{Ph}\mathbf{1}_{Tb}/\mathbf{L_{NH2}}(\boldsymbol{R})/\mathbf{SiO_2}$ (blue), and $^{Ph}\mathbf{1}_{Tb}/\mathbf{L_{NH2}}(\boldsymbol{S})/\mathbf{SiO_2}$ (red) (at 20 K). Solid lines: magnitude; dotted lines: imaginary parts.