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ARTICLE TYPE

# Lanthanide Supramolecular Helical Diastereoselective Breaking Induced by Point Chirality: Mixture or *P*-Helix, *M*-Helix

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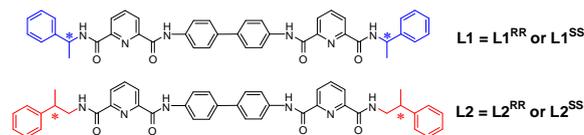
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The self-assembly of lanthanides (europium or lanthanum) bimetallic triple helicates from two closely related chiral ligands, resulted in very different supramolecular phenomenon. One gave rise to significantly diastereoselective formation of a triple helicate, whereas the other lead to diastereoselective breaking to generate a mixture of *P* and *M* diastereomers in ~ 1:1.1 ratio. A first X-ray crystal structure of a chiral ligand based lanthanide triple-helicate indicates that successive CH/ $\pi$  interactions were found to maintain the supramolecular helical structure.

Self-assembly of lanthanide supramolecular systems, particularly multimetallic helicates, have received intensive attention because of their fascinating spectroscopic and magnetic properties.<sup>1-5</sup> Helicates are intrinsically chiral, possessing either *P* or *M* helicity. Control of these stereoselectivity<sup>6-9</sup> is a key issue in these self assemblies, in particular to develop chiral functional materials such as chiroptical probes<sup>10</sup>, molecular switches<sup>11,12</sup> and sensors.<sup>4,5,13</sup> Since lanthanide ions are known to have variable coordination numbers ( $6 \leq CN \leq 12$ ), kinetically labile and poor stereochemical preferences,<sup>14</sup> the precise prediction and control of resulting stereoselectivity of lanthanide supramolecular assemblies is still an important and challenging issue. Research in this area have led to a number of unique structures of chiral lanthanide assemblies appearing in various literatures over the past decade.<sup>14</sup> However, the driving force and mechanistic control in achieving stereoselectivity remains unclear, and hence there is a need for more studies to elucidate this phenomena. For the most intensively investigated types of lanthanide assemblies: triple-stranded bimetallic helix, Ln<sub>2</sub>:L<sub>3</sub>, stereoselective formation has been examined by introduction of a predispose point chiral moiety (point chirality) on to the ligand. The challenge is to design a suitable point chirality so that it can be transferred to the two metal-centers and hence induce an overall helical sense significantly selective of either *P* or *M*. The control of this point-to-helical chirality transfer is difficult and hence diastereoselective formations have been mostly limited to a few reported examples.<sup>10,15,16,17</sup>

We are interested in discovering new type of chiral supramolecule as a potential chiroptical probe for biological and sensing applications. Because of the importance in controlling helical stereoselectivity in lanthanide supramolecular assemblies

for developing (real) functional probes, we, herein, intended to use four new linear biphenyl-linked chiral bis-tridentate ligands,<sup>18</sup> **L1** and **L2** (scheme 1, both ligands with *R,R* or *S,S* configuration at chiral carbons), in which **L2** has a point chirality that is one carbon unit farther apart from the chelating tridentate unit than **L1** to contribute to the understanding of controlling helicity. Upon complexation with lanthanide ions, relationships between the steric factors and stereoselective formation of Ln<sub>2</sub>:L<sub>3</sub>, triple helix structures, which is rarely explored are investigated.



Scheme 1. Ligands (**L** = **L1** or **L2**) used for studying stereoselective formation behavior

Stereoselective behavior of system with chiral ligand can be easily monitored by NMR as the resulting helicates are diastereomers. This behavior is generally difficult to be monitored with the use of achiral ligands as shown by previous studies because the *P* and *M* isomers are normally enantiomers.<sup>19</sup> Upon metals chelation with europium or lanthanum, our preliminary investigations surprisingly indicated that the stereoselective behavior of the metals with these two ligands are dramatically different. **L1** was found to give almost complete diastereoselective formation of a single diastereomer; whereas **L2** was found to form a mixture in almost equal amounts of *P* and *M* isomers. In other words, **L2** failed to induce diastereoselective control in the supramolecular formation process. In addition, our system is unique as the biphenyl linker is one degree of rotation freedom lack, which supposes to be difficult to achieve helical twist, when compares with other common ligands for helical formation.<sup>5,18</sup>

Ligands **L1** and **L2** were designed to be based on two pyridine-2,6-dicarboxamide (pcam) moieties, which are known to form stable nine-coordinated lanthanide complexes.<sup>20</sup> In the formation of bimetallic helicates, the two pcam moieties are connected with a rod-like biphenyl linker. Although the linker are linear, ligands with this linear linker has been demonstrated to be successful in helical enclosure of two 6-coordinated transition metals to form a bimetallic triple helical structure.<sup>21</sup> In our ligand helix design, we decided to investigate whether this type of

linker was suitable to form bimetallic triple helicate with metals that have a much more diverse coordination range, i.e. lanthanide ions. The two ligands (supporting information) were synthesized in two-steps using generic HATU peptide coupling reactions.<sup>22</sup> The <sup>13</sup>C NMR spectra of the ligands shows a total of fifteen aromatic and carbonyl carbon signals for both **L1** and **L2**, indicating a dynamically average C<sub>2</sub>-symmetric behavior of these ligands in solution. **L2<sup>RR</sup>** was further characterized with X-ray structure. The pyridine ring and its neighbor carbonyl-oxygens exhibit transoid conformations about the interannular C–C bonds (Figure S1).

A hypothesis of optimal 3 to 2 stoichiometric ratio of the ligands to europium ion for bimetallic triple helix formation was tested by monitoring changes that occurred with titration experiments. For **L1<sup>RR</sup>**, UV-Vis titrations with Eu(OTf)<sub>3</sub> (from 0 to 2 equiv.) in a mixture of CHCl<sub>3</sub>/MeOH/MeCN (73:3:24, v/v) showed a progressive decrease in ligand absorption (peak at 326 nm) with a simultaneous smooth evolution of a absorption peak for the helicate (peak at 346 nm) with a single sharp end point at ~ 0.65 (Figure S2). The observation of three isosbestic points at 334 nm, 259 nm and 229 nm (not well defined) suggests the existence of two absorbing species, the uncoordinated **L1<sup>RR</sup>** and its corresponding complex, in solution.<sup>23,24</sup> The course of complex formation was also followed with <sup>1</sup>H NMR (400 MHz) titration of ligand **L1<sup>RR</sup>** with Eu(OTf)<sub>3</sub> (Figure 1). Upon addition of Eu(OTf)<sub>3</sub>, a signal at 1.72 ppm (CH<sub>3</sub>- of **L1<sup>RR</sup>**) gradually decreased and a new signal at 1.79 ppm in the aliphatic region progressively increased, which is most likely of stereoselective formation of one helicate (scheme 2a). All the signals from the ligand disappeared when 0.66 equiv. of Eu(OTf)<sub>3</sub> was added. The signals of the resulting helicate are broad due to the paramagnetic property from the europium. New species, corresponding to a signal at 0.76 ppm, also appeared when additional Eu(OTf)<sub>3</sub> was added further.

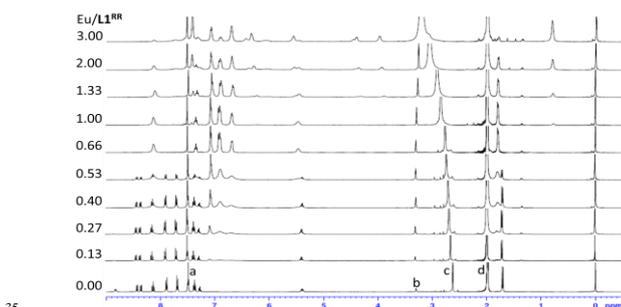
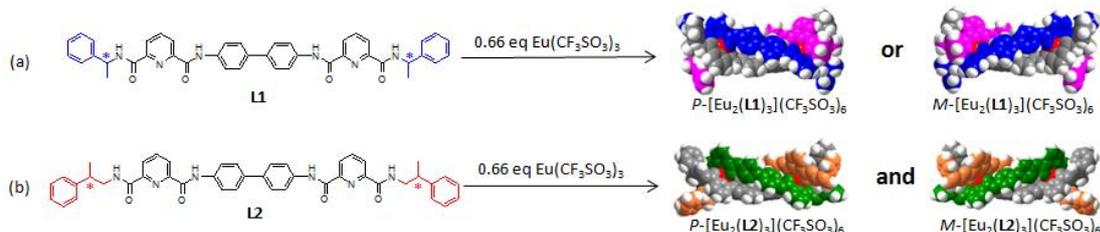


Figure 1. Variation in <sup>1</sup>H NMR spectra upon titrating **L1<sup>RR</sup>** ( $5.11 \times 10^{-3}$  M in 75:5:20, v/v/v, of CDCl<sub>3</sub>/CD<sub>3</sub>OD/CD<sub>3</sub>CN) with Eu(OTf)<sub>3</sub> (0.271 M in CD<sub>3</sub>OD) at 296 K. (Peaks that are marked as a, b, c and d are from the residual solvents of CHCl<sub>3</sub>, MeOH, H<sub>2</sub>O and MeCN, respectively.)

#### Scheme 2. Stereoselective formation behaviour of **L1** and **L2**



For the ligand **L2**, a similar observation with UV-Vis titrations of **L2<sup>SS</sup>** with Eu(OTf)<sub>3</sub> was obtained (Figure S3). End point was found to be ~ 0.68 equiv. of Eu(OTf)<sub>3</sub>. <sup>1</sup>H NMR titrations also exhibited a complete disappearance of signals from **L2<sup>SS</sup>** after 0.66 equiv. of Eu(OTf)<sub>3</sub> was added (Figure S4). Interestingly, two new set of signals appeared at 0.97 and 1.40 ppm with integration ratio ~ 1:1.1, but signal at 1.37 ppm corresponding to the CH<sub>3</sub>- of **L2<sup>SS</sup>** disappeared during titration range from 0 to 0.66 equiv. of Eu(OTf)<sub>3</sub>. Two diastereoselective helicates were formed with slight stereochemical bias (scheme 2b). Upon continuous addition of Eu(OTf)<sub>3</sub>, another new signal at 0.82 ppm emerged corresponding to the consumption of the species assigned to the signals of 0.97 and 1.40 ppm which is indicative of formation of another new specie. This study also confirmed our hypothesis of a 3 ligand and 2 metal ratio structural assembly.

The corresponding europium complexes with **L1** and **L2** were then synthesized by reacting three equivalent of **L1** or **L2** to two equivalent of Eu(OTf)<sub>3</sub>. Single crystal of [Eu<sub>2</sub>(**L1<sup>SS</sup>**)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>6</sub> was obtained by slow evaporation of the complex in acetonitrile. To the best of our knowledge, it is the first single X-ray characterized chiral ligand based lanthanide bimetallic triple helicate. The crystal structure is shown in Figure 2.<sup>25</sup>

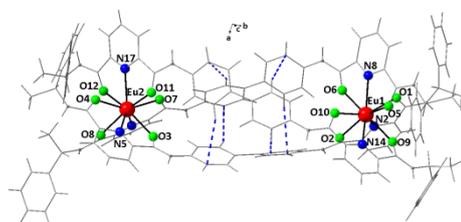


Figure 2. Crystal structure (highlighted only the atoms involving coordination polyhedral; dashed lines indicate CH/π distances < 3.20 Å) of cationic [Eu<sub>2</sub>(**L1<sup>SS</sup>**)<sub>3</sub>]<sup>6+</sup>.

The structure shows three ligands **L1<sup>SS</sup>** which wrap around two Eu(III) centers in the same Δ-configuration, and result in an overall P helical sense. A total of five strong (2.874(8) to 2.989(9) Å) and one weaker (3.154(6) Å) CH/π interaction<sup>26</sup> are found to stabilise the construction of the helical structure. In order to form helical structure successfully, the three ligand strands adopt successive interannular C–N (in the range of 7.19–13.83°) and C–C (in the range of 20.29–35.33°) bonds rotation between the two Eu centers. The distance along a pseudo-C<sub>3</sub> axis passing through the two Eu centers is 15.055(1) Å, which is found to be longer than those for previously reported lanthanide dinuclear triple helicates.<sup>2</sup> For [Eu<sub>2</sub>(**L1<sup>SS</sup>**)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>6</sub>, each of the Eu centers can be described to be in a distorted tricapped trigonal prismatic geometry. For each Eu center, the three pyridyl atoms occupied equatorial plane which are sandwiched by two faces, containing the six oxygen atoms of the amide groups, in the trigonal prism. For the two Eu centers, the distortion from the

trigonal prismatic geometry can be observed as the large twisting angles between the two faces are 18.81° (Eu1) and 21.23° (Eu2), respectively. Selected bond lengths and angles are given in Chart S1 and Table S1. Single crystal of  $[\text{Eu}_2(\text{L2}^{\text{RR}})_3](\text{CF}_3\text{SO}_3)_6$  was also obtained for X-ray crystallography. However, the quality of the crystals was not suitable for detail analysis, but the overall helical structure was still observable. (Figure S5).<sup>25</sup>

$^1\text{H}$  and  $^{13}\text{C}$  NMR were then performed to further characterize the helicates. For the  $[\text{Eu}_2(\text{L1}^{\text{RR}})_3](\text{CF}_3\text{SO}_3)_6$ , although all the signals in  $^1\text{H}$  NMR spectrum for this helicate were broad (Figure S6), the number of integration matched the corresponding  $C_2$ -symmetric nature of the free ligand. However, from this study alone, conclusive presence of the total number of species could not be confirmed, even from further studies by variable temperature NMR experiments. Upon decreasing the temperature to  $-35^\circ\text{C}$ , the signals were still too broad to determine a clear number of species (Figure S7). A clearer picture on this issue was obtained with  $^{13}\text{C}$  NMR. Primarily, only one set of signals was observed (Figure S8). The total number of signals (17 signals) matches to that for the  $C_2$ -symmetry of ligand  $\text{L1}^{\text{RR}}$ , indicating high symmetric property of the helicates. The corresponding La helicate was also prepared because of its diamagnetic nature. NMR comparison with the corresponding Eu helicate was found to be informative. The La helicate was also synthesized via the same method as the Eu helicate.  $^1\text{H}$  NMR shows clearly that one major species was present (Figure S9), which indicates the presence of one time-average and highly symmetric species on the NMR time scale. Studies on  $\text{L2}$  were also performed. To our surprise, investigation of  $[\text{Eu}_2(\text{L2})_3](\text{OTf})_6$  shows a very different observation compared to  $\text{L1}$ . For some of the signals of the  $^1\text{H}$  (Figure S10) and  $^{13}\text{C}$  (Figure S11) NMR of  $[\text{Eu}_2(\text{L2}^{\text{RR}})_3](\text{CF}_3\text{SO}_3)_6$ , two sets of peaks were observed. Based on the well resolved pair of signals from the methyl protons<sup>27</sup> (0.84 and 1.26 ppm) in  $^1\text{H}$  NMR, their ratio showed to be in  $\sim 1:1.1$ . These indicated a very high probability of the signals arising from two species. Actually, the two species seem to be in a dynamic exchange process as shown by signals shifting to one another at higher temperature (Figure S12). In addition, the investigation of its diamagnetic analogous La helicate also showed two sets of signals in a ratio of  $\sim 1:1.1$  which is similar to the case in  $[\text{Eu}_2(\text{L2}^{\text{RR}})_3](\text{CF}_3\text{SO}_3)_6$  (Figure S13). All the signals are much broader when compare with its La counterpart of  $\text{L1}$ , which most probably is due to the existence of a dynamic exchange process as shown by coalescence of signals at higher temperature  $^1\text{H}$  NMR (Figure S14).

Solution circular dichroism (CD) measurement was also performed to help verify the nature of the species of  $[\text{Eu}_2(\text{L1})_3](\text{CF}_3\text{SO}_3)_6$  and  $[\text{Eu}_2(\text{L2})_3](\text{CF}_3\text{SO}_3)_6$  which resulted in the very different NMR observation. In CD studies, these complexes also exhibit very distinct CD spectra from each other. For the  $[\text{Eu}_2(\text{L1})_3](\text{CF}_3\text{SO}_3)_6$ , five CD signals, peaks at 379, 333, 283, 252 and 216 nm, with strong Cotton effects from  $\pi \rightarrow \pi^*$  transitions are detected in the range of 200 to 450 nm (Figure 3). As expected, mirror image of CD spectra is observed for the Eu helicates from the opposite chiral  $\text{L1}^{\text{RR}}$  and  $\text{L1}^{\text{SS}}$ . In addition, very similar CD spectra for the corresponding La helicates are observed (Figure S15).

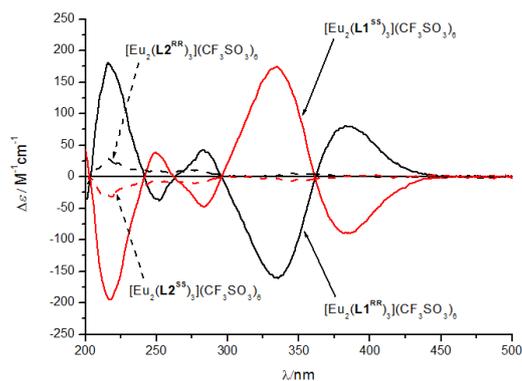


Figure 3. CD spectra of  $[\text{Eu}_2(\text{L1})_3](\text{CF}_3\text{SO}_3)_6$  ( $3.23 \times 10^{-5}$  M) and  $[\text{Eu}_2(\text{L2})_3](\text{CF}_3\text{SO}_3)_6$  ( $3.52 \times 10^{-5}$  M) in MeCN.

For helicates of  $\text{L2}$ , a completely different pattern of CD spectra are obtained for the  $[\text{Eu}_2(\text{L2})_3](\text{CF}_3\text{SO}_3)_6$ . Significant decrease in CD signals are observed. The extent of attenuation depends on wavelengths which are roughly shown to be 96.8% (379 nm), 99% (333 nm), 77% (283 nm), 69% (252 nm) and 84% (216 nm) of decrease in signals, respectively. Similar attenuation is observed for the corresponding La complexes (Figure S15). Similarity of CD spectra for the Eu and La helicate indicates that the helical behavior for the helicates are alike. In correlation to results from NMR, we can tentatively assign that diastereomeric  $P$  and  $M$  species were formed based on  $\text{L2}^{\text{RR}}$  or  $\text{L2}^{\text{SS}}$ . The two isomers induce opposite CD signals in almost identical amplitude at the corresponding wavelengths, resulting in much weaker CD observations.

Luminescent properties of these newly synthesized Eu chiral helicates were investigated to study its potential as luminescence materials in both solid (Figures S16–27) and solution state (Figures S28–39). In general, both helicates displayed characteristic narrow Eu red emission lines (594; 615 and 619; 687, 697 and 704 nm) corresponding to decay from the first excited state ( $^5\text{D}_0$ ) to the ground multiple states ( $^7\text{F}_J$ ,  $J = 1, 2,$  and  $4$ , respectively) attributed to energy transfer from the triplet states of the pyridyl or phenyl chromophores of the ligand strands. The highest intensity peak was observed at 615 nm, typically observed from europium which is from the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  band. The presence of an emission peak at 581 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ) indicates that the overall symmetry of the complex is  $C_3$ . No significant difference in the relative spectral intensity upon different wavelength excitations (342 to 363 nm) were observed.

Excited state decay of the emission showed that the helicates were best fitted to a mono-exponential decay, suggesting the presence of a single or very similar luminescent specie in solution, supporting the NMR studies. Lifetimes of  $\sim 0.2$  to  $0.4$  ms are shorter than those of typical europium complexes (Table S2).<sup>18</sup> The sensitized energy was probably deactivated via back energy transfer from  $^5\text{D}_2$  to ligand based on a preliminary investigation with a Gd complex (Figures S40–42). Luminescence study with d-MeCN showed no significant enhancement of emission (Figure S43–S44), and implies that the coordination sphere of Eu was probably not affected by the solvent MeCN.

## Conclusions

In summary, we have demonstrated that the diastereoselective and diastereoselective breaking supramolecular formation behavior (*P* and *M* helicity) of the lanthanide triple helix is extremely sensitive to small structural variations in the ligands. With the use of the traditional non-preferable helical twisting linear ligands, significant diastereoselective and non-diastereoselective formation of bimetallic triple helix are observed by just simply and slightly extending the point chirality from the two metal centers, and hence significantly altering the ability of chirality transfer, which is the first time observed with chiral lanthanide dinuclear triple helicates. This matter is important as it helps elucidate chiral selectivity for formation of lanthanide supramolecular compounds. Hence allowing manipulation of desired properties such as optical and magnetic for potential use in applications either for material or in the biological regime.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Detail experimental procedures, characterizations, preliminary circularly polarised luminescence studies (CPL) and crystallographic data are available in supporting information. See DOI: 10.1039/b000000x/

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