Sorting Phenomena and Chirality Transfer in Fluoride-Bridged Macrocyclic Rare Earth Complexes

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ABSTRACT: The reaction of fluoride anions with mononuclear lanthanide(III) and yttrium(III) hexaaza-macrocyclic complexes results in the formation of dinuclear fluoride-bridged complexes. As indicated by X-ray crystal structures, in these complexes two metal ions bound by the macrocycles are linked by two or three bridging fluoride anions, depending on the type of the macrocycle. In the case of the chiral hexaaza-macrocycle L1 derived from trans-1,2-diaminocyclohexane, the formation of these \( \mu_2 \)fluorido dinuclear complexes is accompanied by enantiomeric self-recognition of macrocyclic units. In contrast, this kind of recognition is not observed in the case of complexes of the chiral macrocycle L2 derived from 1,2-diphenylethylenediamine. The reaction of fluoride with a mixture of mononuclear complexes of L1 and L2, containing two different Ln(III) ions, results in narcissistic sorting of macrocyclic units. Conversely, a similar reaction involving mononuclear complexes of L1 and complexes of achiral macrocycle L3 based on ethylenediamine results in sociable sorting of macrocyclic units and preferable formation of heterodinuclear complexes. In addition, formation of these heterodinuclear complexes is accompanied by chirality transfer from the chiral macrocycle L1 to the achiral macrocycle L3 as indicated by CPL and CD spectra.

INTRODUCTION

Chiral structures and chiral recognition phenomena are fundamental features of molecular biological systems, and chirality is a central issue in various areas of organic and inorganic chemistry. For instance, chiral metal complexes and chiral supramolecular assemblies are studied as enantioselective catalysts, chiroptical probes, and nonlinear optical materials. Similarly, the recognition and self-organization phenomena characteristic for complex biological systems have triggered research in many areas of chemistry. Both social self-sorting (self-discrimination) and narcissistic self-sorting (self-recognition) are examples of such phenomena that attract increasing attention.1–33

Chiral sorting corresponds to enantiomeric self-recognition or enantiomeric self-discrimination, and these processes have been documented for supramolecular systems,1–6 metal complexes,7–21 and organic systems, including macrocyclic compounds.22–33 Chiral sorting phenomena are most often demonstrated for solid state, while examples of enantiomeric self-recognition well documented for solutions of metal complexes are less common. Another important issue in the synthesis of elaborate enantiopure metal complexes or supramolecular assemblies is chirality transfer,32–35 e.g., the transmission of chiral information from enantiopure ligands to metal centers. While there are many chiral transition metal complexes with well-defined stable configurations, the control over chirality of lanthanide complexes, in particular polynuclear complexes,54–36,44–58 is more difficult due to the lack of spatial preferences, lability, and high-coordination numbers of these ions. For similar reasons recognition and self-sorting phenomena4–12,20,21 in lanthanide systems are not so well explored in comparison with the systems based on stable organic compounds or more rigid and inert transition metal complexes.

Here we describe fluoride derivatives of lanthanide(III) and Y(III) (denoted as Ln(III)) complexes of hexaaza-macrocycles L1–L3 derived from 1,2-diformylpyridine and various diamines (Figure 1). We show that dinuclear complexes of this type may contain two different macrocyclic units and that their formation is governed by self-sorting phenomena. By using circularly polarized luminescence (CPL) and circular dichroism (CD) spectroscopy, we also demonstrate chirality transfer from chiral to achiral macrocycle in these mixed dinuclear complexes.

The number of well-defined molecular lanthanide(III) complexes containing fluoride ligands is limited due to the...
tendency to precipitate insoluble Ln(III) fluoride salts as well as due to the difficulty in controlling the coordination sphere of these labile ions. In particular, macrocyclic ligands based on tetraaza-cyclen framework strongly bind lanthanide(III) ions and form stable fluoride derivatives. Some of these cyclen-based complexes are mononuclear and contain terminal fluoride anions, while other are dinuclear where two macrocyclic units are linked by a single linear $\mu_2$-fluorido bridge. The binding of fluoride by these cyclen-based Eu(III) and Tb(III) complexes has been studied in the context of sensing of fluoride anions by using luminescence spectroscopy. In addition, a terminal fluoride anion bound in the axial position in cyclen-based Dy(III) complexes and in polychelate Dy(III) complexes generates high magnetic anisotropy of the Dy(III) ions and enhances single-ion magnet (SIM) properties. It has been also suggested that the Dy(III) complex with a hexaaza-macrocycle derived from 1,2-diacetylpyridine and ethylenediamine should exhibit exceptional magnetic anisotropy and SIM behavior.

**RESULTS AND DISCUSSION**

**Mononuclear Lanthanide(III) Complexes of Macrocyle L2.** The new enantiopure rare earth(III) complexes of macrocycle L2 have been obtained in a template synthesis from the lanthanide(III) (Ln = Pr, Nd, Tb) or yttrium(III) chlorides, 2,6-diformylpyridine, and (1$R$,2$R$)-1,2-diphenylethylenediamine or (1$S$,2$S$)-1,2-diphenylethylenediamine in the same manner as it was reported for La, Eu, and Dy complexes. The crystal structure of the [La(L2$R$)Cl$_3$]·2.5MeOH·0.5H$_2$O complex, isomorphic to the previously reported Ce(III) derivative, shows 9-coordinate La(III) ion bound by the six nitrogen atoms of the macrocycle and three axial chloride anions (Figure 2). The macrocycle L2 is relatively flat in this complex with moderate helical twist of the pyridine fragments and very small folding of the macrocycle reflected by almost linear arrangement of the two pyridine nitrogen atoms and the central metal ion. In contrast, in the related Tb(III) complex the macrocycle is not only helically twisted but also sizably folded (Figure 3). The asymmetric unit of the {[Tb(L2$S$)Cl$_3$(MeOH)]}$^+$ and {[Tb(L2$S$)Cl$_3$(H$_2$O)]}$^+$ of the {[Tb(L2$S$)Cl$_3$(MeOH)][Tb(L2$S$)Cl$_3$(H$_2$O)]}Cl$_2$·9MeOH·H$_2$O crystal (hydrogen atoms omitted for clarity). Gray: C atoms; blue: N; green: Cl; red: O; violet: Tb.
The NMR spectra of the Pr(III), Nd(III), Tb(III), and Dy(III) complexes of L2 cover a wide range of chemical shifts and show very broad lines (in particular in the case of Tb(III) and Dy(III) derivatives) in accord with the binding of the paramagnetic metal ion in the center of the macrocycle. The $^1$H NMR spectra of the [Ln(L2)Cl3] complexes consist of seven signals of the ligand L2. This number of lines indicates an effective D$_3$ symmetry of the complexes reflecting dynamic averaging of the structures observed in the crystalline state. This process most likely results from fast axial ligand exchange on the NMR time scale.

Because the [Ln(L2)Cl$_3$] complexes can be obtained in enantiopure form and Eu(III) and Tb(III) complexes may be luminescent, we were interested in CPL activity of the complexes upon UV excitation (Figure 4). The luminescence spectra for the 5D$_0$→7F$_1$ and 5D$_0$→7F$_2$ transitions, 5D$_0$→7F$_1$ for Eu(III) and 5D$_0$→7F$_2$ for Tb(III), where one predicts the CPL would be large. We were able to measure a CPL signal for the set of enantiomeric pairs of the chiral Eu(III)-containing compounds upon UV excitation (Figure 4). The luminescence dissymmetry ratio, $g_{\text{num}}$ is defined as follows:

$$g_{\text{num}} = \frac{\Delta I}{I} = \frac{I_I - I_R}{I_I + I_R}$$

where $I_I$ and $I_R$ refer respectively to the intensity of left and right circularly polarized light.

For the pair of the Eu(III) complexes [Eu(L$_2^6$)Cl$_3$] and [Eu(L$_2^8$)Cl$_3$], we were able to record opposite CPL spectra, which show the Eu(III)-centered polarized emission following excitation at about 333–329 nm (nondeuterated solutions) and 329–330 nm (deuterated solutions), respectively. The transition that we studied is the magnetic dipole allowed transitions, 5D$_0$→7F$_1$ for Eu(III). In addition, we also recorded the CPL activity for the (Eu) 5D$_0$→7F$_2$. The CPL activity observed from the two enantiomeric forms of the Eu(III)-containing complexes is roughly similar, with a magnitude of the $g_{\text{num}}$ values a little smaller for the samples measured in deuterated versus nondeuterated 2:1 chloroform/methanol solutions. The $g_{\text{num}}$ values are −0.05/+0.05, +0.05/−0.05, −0.03/+0.03 versus −0.05/+0.05, +0.07/−0.06, −0.03/+0.04 for the three components (~591, 596, and 618 nm) of the CPL spectra for the Eu(III) complexes of the L$_2^6$/L$_2^8$ enantiomers of the macrocycle, respectively (Figure 4).

It was not possible to record the CPL activity of the two enantiomeric forms of the Tb(III)-containing complex L2 in nondeuterated and deuterated 2:1 chloroform/methanol solutions at concentrations of 1 and 10 mM. The intensity was too weak, suggesting that there is most likely an effective back-transfer from the Tb(III) to the ligand and/or an inefficient intersystem crossing between the singlet and triplet states of the ligand taking place for the Tb(III)-containing complexes. However, the observation of the CPL activity for the Eu(III)-containing compounds tends to favor an efficient Tb(III) back-transfer phenomenon.

Crystal Structures of Fluoride-Bridged Homodinuclear Ln(III) Complexes of Macrocycles L1–L3. The dimeric [Ln$_2$(L1)$_2$(μ$_2$-F)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ complexes have been obtained from the mononeric nitrate derivatives [Ln(L1)(NO$_3$)$_2$](NO$_3$) by addition of a stoichiometric amount of potassium fluoride or tetraethylammonium fluoride, NE$_4$F. The crystal structure of the Lu(III) complex [Lu$_2$(L1)$_2$(μ$_2$-F)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·CHCl$_3$·3H$_2$O (Figure 5, Figures S1 and S2) indicates two parallel macrocyclic units linked by two bridging fluoride anions. The crystal of this compound contains the cationic complex [Lu$_2$(L1)$_2$(μ$_2$-F)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·CHCl$_3$·3H$_2$O (Figure 5). The macrocyclic ligand L1 in these complexes is helically twisted, and the direction of the helical twist is determined by the configuration at the asymmetric carbon atoms of the diaminocyclohexane units. Thus, the twist of the two pyridine rings of L1 corresponding to the mutual $\Delta$ orientation is associated with the L1$^3$ enantiomer of the ligand, while the opposite $\Delta$ twist of these units is associated with the L1$^5$ enantiomer.

The preliminary structural data for the [Dy$_2$(L1)$_2$(μ$_2$-F)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·CHCl$_3$·nH$_2$O crystal show that its structure is very similar (isostructural) to the above Lu(III) complex (Figure S3). The structure of Eu(III) complex of [Ln$_2$(L1)$_2$(μ$_2$-F)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ type could not be satisfac-
torily solved due to crystal quality; however, the crude model shows its isostructurality to the Lu(III) crystal.

Similar fluoride-bridged dinuclear complexes can be obtained from the monomeric chloride derivatives [Ln(L1)Cl3]. For instance, the reaction of Yb(III) complex of this type with 1.5 equiv of NEt4F results in isolation of crystals of the 

$$[\text{Yb}_2(L_1 R)_2(\mu_2-F)_2F(H_2O)]Cl_3 \cdot 3.5\text{MeOH} \cdot 4.5\text{H}_2\text{O complex}$$

where one of the Yb(III) ions contains additional terminal fluoride anion in the axial position, while the other Yb(III) contains an axial water molecule (Figure 6 and Figure S4). In the crystal lattice of this complex the complex cation 

$$[\text{Yb}_2(L_1 R)_2(\mu_2-F)_2F(H_2O)]^{3+}$$

is linked by hydrogen bonds linking the fluoride and axial water molecules belonging to different complex cations, which leads to formation of supramolecular helical chains (Figure S5).

Dimeric fluorido-bridged complexes are also formed in the reactions of mononuclear nitrate-type complexes [Ln(L3)-(NO3)2]2{(NO3)2} of the macrocycle L3 derived from ethylenediamine. The molecular structure of the cationic complex

$$[\text{Y}_{2}(L_{3})_{2}(\mu_{2}-F)_{2}(\text{NO}_{3})_{2}]^{2+},$$

present in the crystal structure of the dimeric Y(III) complex of L3, is analogous to the above-discussed complexes of L1 (Figure 7 and Figure S6). The conformations of the chiral macrocycle L1 and the achiral macrocycle L3 in these fluoride-bridged complexes are similar. Importantly, the achiral ligand L3 is helically twisted in the complexed form, and thus, it assumes a chiral conformation. Within the fluorido-bridged complex

$$[\text{Y}_{2}(L_{3})_{2}(\mu_{2}-F)_{2}(\text{NO}_{3})_{2}]^{2+},$$

(NO3)2-CHCl3-MeOH-H2O both macrocyclic units adopt the same direction of helical twist, either ΔΔ or ΛΛ, and the centrosymmetric crystals of this complex contain both forms as a racemic mixture.

The reaction of the complex of the macrocycle L2, [La(L25)Cl3], with NEt4F results in a different kind of dimer in comparison with the dimeric complexes of macrocycles L1 and L3 discussed above. Thus, the X-ray crystal structure of the obtained product

$$[\text{La}_{2}(L_{25})_{2}(\mu_{2}-F)_{2}(\text{H}_{2}O)]\text{Cl}_3 \cdot 5\text{MeOH} \cdot 4.5\text{H}_2\text{O}$$

shows a dimeric structure where three fluoride anions bridge the La(III) ions (Figure 8 and Figure S7). In contrast, in the dimeric Ln(III) complexes of macrocycles L1 and L3, metal ions are linked by only two μ2-F− bridges.

While dinuclear molecular Ln(III) complexes of the di-μ2-fluorido type are known, to the best of our knowledge this is a first example of a molecular tri-μ2-fluorido dinuclear Ln(III) complex. The Ln2(μ2-F)3 structural motif can be found, however, in the Ln(III)-containing cluster, oligomeric or polymeric compounds. The La–La distance in the complex cation

$$[\text{La}_{2}(L_{25})_{2}(\mu_{2}-F)_{2}(\text{H}_{2}O)]^{2+}$$

is 3.71 Å, which is similar value to the values of the corresponding distances 3.66, 3.71, and 3.66 Å observed for the Lu(III), Y(III), and Yb(III) dinuclear complexes of L1 and L3, discussed above. The two macroyclic units in this complex are close to each other, and
phenyl rings at the periphery of macrocycle L2 are rotated in such a way that minimizes steric interactions (Figure 9). In this dimeric complex the macrocyclic units are bent away from the bridging fluorides. In contrast, in the discussed above fluoride-bridged dimers containing macrocycles L1 or L3, the macrocyclic units are twisted but practically not bent.

**NMR Spectra of Fluoride-Bridged Homodinuclear Ln(III) Complexes of Macrocycles L1−L3.** The NMR spectra of paramagnetic macrocyclic Ln(III) complexes may be dramatically changed upon exchange of anions bound in axial positions,91,92 including fluoride.67,68,71 The number of $^1$H NMR signals observed for the dimeric [Ln$_2$(L1)$_2$(μ$_2$-F)$_3$F(H$_2$O)]$_2^+$ complexes (15 signals, Figure 10 and Figure S8) is increased in comparison with that observed for the starting nitrate derivatives [Ln(L1)(NO$_3$)$_2$](NO$_3$) (eight signals). This observation, points to the switch from the effective $D_2$ symmetry of the macrocycle in the starting complexes to the $C_2$ symmetry in the dimer, in accord with the X-ray crystal structures. The lower symmetry of the macrocycle is also confirmed by correlation pattern in the COSY spectrum of the dinuclear Eu(III) complex (Figure S8). Moreover, the range of chemical shifts is greatly changed, particularly for the Yb(III) complexes, where the $^1$H NMR spectrum of the starting mononuclear complex [Yb(L1)(NO$_3$)$_2$](NO$_3$) spans the range of 1 to 26 ppm, while that of the dimeric fluoride derivative spans the range of −49 to 89 ppm (Figure S9). For macrocyclic Yb(III) complexes this kind of profound change of spectral pattern does not arise primarily from the different conformations of the ligand. Instead, it reflects the change of the dominant dipolar (pseudocontact) contribution$^{93–98}$ to the paramagnetic shift caused by the exchange of axial ligands.$^{91,92}$ This effect, in turn, arises from the change of the parameters of the magnetic susceptibility tensor accompanying the change of
crystal field at the paramagnetic lanthanide(III) center caused by the replacement of the nitrate or chloride axial ligands with fluoride anions.

The formation of macrocyclic fluoride-bridged Ln(III) complexes in solution was monitored by using 1H NMR titration experiments. Gradual addition of solution of sodium fluoride or tetrachloroammonium fluoride to mixed methanol/chloroform solutions of [Ln(L1)](NO3)2(NO3) (Ln = Eu, Dy, Yb, Lu, Y) complexes results in subsequent formation of at least three new forms of macrocyclic complexes (Figure 10, Figures S9 and S10). These experiments indicate exchange of axial nitrate anions for fluoride anions. For instance, in the case of Eu(III) derivative addition of up to 1 equiv of F− results in generation of new complex in slow exchange (on the NMR time scale) with the starting complex (Figure 10). This new spectrum is identical with that of the synthesized [Eu2(L1)2(μ2-F)2(NO3)2]2+ complex. The addition of more equivalents of fluoride salts brings about further spectral changes consistent with the generation of at least two new fluorido-bridged macrocyclic complexes, most likely corresponding to complex cations with additional terminal fluoride anions: [Ln2(L1)2(μ2-F)2F(NO3)2]2+ and [Ln2(L1)2(μ2-F)2F]2+.

Similar results were obtained in 1H NMR titration experiments with the [Ln(L1)Cl3] series of complexes (Figure S10). In this case various fluorido-bridged dinuclear species may coexist in solution. For instance, addition of 1.3 equiv of NEt4F to the mixed methanol/chloroform solution [Yb(L1)]2-Cl] results in a mixture of three dinuclear species such as [Yb2(L1)2(μ2-F)2Cl2]2+, [Yb2(L1)2(μ2-F)2FCl]2+, and [Yb2(L1)2(μ2-F)2F]2+. Gradual addition of fluoride anions to the solutions of Ln(III) complexes of macrocycles L2 and L3 based on 1,2-diphenylethylenediamine and ethylenediamine, respectively, also brings about substantial NMR changes. However, the 1H NMR lines of the paramagnetic derivatives generated after addition of fluoride to the solutions of [Ln(L2)Cl3] or [Ln(L3)Cl3] are much broader in comparison with those of analogous complexes of L1, and this effect precluded more detailed analysis. The additional line broadening reflects more flexible systems with faster axial ligand exchange and/or conformational changes.

**Formation of Fluoride-Bridged Heterodinuclear Complexes and Self-Sorting of Macrocyclic Units in Solution.** The dinuclear nature of the fluoride derivatives of macrocyclic Ln(III) complexes present in solution may be verified by using two different metal ions. In the 1H NMR titration experiments fluoride anions have been added to a mixture of two different mononuclear macrocyclic complexes containing ions Ln(III) and Ln(III). If the dimeric complexes are formed in these solutions, one should observe, apart from the signals of the homodinuclear complexes, additional set of signals corresponding to the heterodinuclear fluoride-bridged complexes. In particular, these new species should be easily discerned in the case of paramagnetic macrocyclic Ln(III) complexes because of the high sensitivity of chemical shifts of these complexes to any structural modifications. In the case of starting mixture of mononuclear complexes of macrocycle L1 of the same chirality, e.g., a mixture of [Yb(L1)3(NO3)2]- (NO3) and [Lu(L1)3(NO3)2]2(NO3)2, indeed the signals of a mixed dimer such as [YbLu(L1)2(μ2-F)2(NO3)2]2+ were observed (Figure 11). In this case the dinuclear Yb−Yb, Yb−Lu, and Lu−Lu fluoride-bridged complexes have been formed roughly in the statistical 1:2:1 ratio. A different result was observed with the initial mixture of complexes of opposite chirality, e.g., [Yb(L1)3(NO3)2][NO3] and [Lu(L1)3(NO3)2]− (NO3) (Figure 11). In this case no heterodinuclear Yb−Lu complex was observed. This result is a proof of enantiomeric self-recognition, i.e., narcissistic self-sorting with respect to helicity of macrocyclic units (Scheme 1). This chiral recognition process was not observed in analogous experiments with complexes of macrocycle L2. In this case new heterodinuclear species were observed for the La−Nd couple irrespective of chirality of the macrocycle. With the mixed couples of complexes containing heavier Ln(III) ion or Y(III) the titration experiments suggest that mainly mononuclear fluoride species are generated because heterodinuclear species were not observed.

In another set of NMR titration experiments mixtures of two mononuclear complexes containing not only two different metal ions but also two different macrocycles were used. In the case of mixtures of complexes [Ln(L1)Cl3] and [Ln′(L2)Cl3] after addition of fluoride no dinuclear Ln−Ln′ species containing two different macrocycles L1 and L2 were observed in 1H NMR spectra irrespective of the chirality of the macrocycles. This result points to narcissistic self-sorting of macrocyclic units L1 and L2 (Scheme 1). Similar results were obtained for the starting mononuclear complexes [Ln(L2)Cl3] and [Ln′(L3)Cl3] pointing to narcissistic self-sorting of macrocyclic units L2 and L3. In contrast, sociable self-sorting of macrocycles L1 and L3 was observed during formation of
resulted in formation of the heterodinuclear [Yb(L1S)Y(L3)]2− complex. Moreover, the macrocycle L3 is based on ethylenediamine lateral chains and is achiral, both its mononuclear complexes [Ln(L3)(NO3)2](NO3) and dinuclear complexes [Ln2L32(μ2-F)2(NO3)2](NO3) do not exhibit CD signals. Nevertheless, the X-ray crystal structures indicate that this macrocycle adopts chiral, helical conformation in its monomeric Ln(III) complexes117 as well as in the dimeric fluoride-bridged complex discussed above. Moreover, both macrocyclic L3 units are of the same chirality within the dimer. Because this homohelical arrangement is analogous to the homochiral formation of dinuclear complexes of L1, it is likely that in the mixed [Ln(L1)Ln′(L3)(μ2-F)2(NO3)2]2+ complex cation the macrocycle L3 has to assume the same direction of helical twist as macrocycle L1 to minimize steric interactions between the two macrocyclic units. The Λ and Δ conformations are equally probable in the dinuclear [Ln2(L3)2(μ2-F)2(NO3)2](NO3)2 complexes of L3. On the other hand, the macrocyclic unit L3 may adopt preferable Δ conformation when it is in close contact with the Δ/L13 macrocyclic unit in the mixed dimer [Ln(L1)Ln′(L3)(μ2-F)2(NO3)2]2+. Conversely, the preferable Λ conformation of L3 may be present in the [Ln(L1′L3)2(μ2-F)2(NO3)2](NO3)2 complex cations. CPL and CD spectra indicate that this kind of chirality transfer from the chiral macrocycle L1 to achiral macrocycle L2 is indeed happening.

Thus, the CPL signal was monitored for the mixture of [Y(L1)(μ2-F)2(NO3)2](NO3)2, [Eu(L3)(μ2-F)2(NO3)2](NO3)2 and [Y(L1′L3)2(μ2-F)2(NO3)2](NO3)2 complexes generated from the mixture of [Eu(L3)(NO3)2](NO3) and [Y(L1′L3)2(NO3)2](NO3) (Figure 12). The transition that was measured for this sample dissolved in deuterated 2:1 chloroform/methanol solution was the magnetic dipole allowed transition 3D0 → 7F2 for Eu(III). In addition, we also recorded the CPL activity for the (Eu)3D0 → 7F2. The g_0 values are −0.05 and +0.04 for the (Eu)3D0 → 7F2 and 3D0 → 7F2 transitions. The observation of an Eu(III)-centered CPL activity clearly indicates that the Eu(III) resides in a chiral nonracemic complex. The signals cannot arise from the enantiopure complex [Y(L1)(μ2-F)2(NO3)2](NO3)2 since it is nonluminescent and CPL silent. They also cannot arise from the Eu(L3)(μ2-F)2(NO3)2]2+ component since, here, Eu(III) resides in a racemic mixture of Λ and Δ conformations of the achiral ligand L3. The conclusion is that CPL activity has to arise from the [Y(L1′L3)2(μ2-F)2(NO3)2](NO3)2 component of the mixture and that the Eu(III) ion in the heterodinuclear complex cation [Y(L1′L3)2(μ2-F)2(NO3)2]2+ is bound by achiral L3 which has assumed only one of the two possible directions of the helical twist (Scheme 3). It should be mentioned that the NMR spectra of the sample used for CPL measurements do not indicate characteristic paramagnetic signals of species where the Eu(III) ion is coordinated to the chiral macrocycle. Thus, the observed CPL signal of Eu(III) does not arise from the metal ion dissociation and scrambling between the L1 and L3 sites.
Similarly, chirality transfer from the enantiopure macrocycle L1 to the achiral macrocycle L3 is confirmed by the CD spectra. As expected, the CDCl3/CD3OD 2:1 v/v solution of the mixture of \([\text{Nd}(L3)(NO_3)_2](NO_3)_2\), \([\text{Eu}(L3)(\mu_2-F)(NO_3)_2](NO_3)_2\), and \([\text{Y}(L1^S)(\mu_2-F)(NO_3)_2](NO_3)_2\) complexes in 2 mM deuterated 2:1 chloroform:methanol at 295 K, upon excitation at 321 nm.

**Scheme 3**

Similarly, chirality transfer from the enantiopure macrocycle L1 to the achiral macrocycle L3 is confirmed by the CD spectra. As expected, the CDCl3/CD3OD 2:1 v/v solution of the mixture of \([\text{Nd}(L3)(NO_3)_2](NO_3)_2\), \([\text{Eu}(L3)(\mu_2-F)(NO_3)_2](NO_3)_2\), and \([\text{Y}(L1^S)(\mu_2-F)(NO_3)_2](NO_3)_2\) complexes in 2 mM deuterated 2:1 chloroform:methanol at 295 K, upon excitation at 321 nm.

**Figure 12.** CPL (upper curves) and total luminescence (lower curves) spectra for the \(5D_0 \rightarrow 7F_1\) and \(5D_0 \rightarrow 7F_2\) transitions of the mixture of \([\text{Y}(L1^S)(\mu_2-F)(NO_3)_2](NO_3)_2\), \([\text{Eu}(L3)(\mu_2-F)(NO_3)_2](NO_3)_2\), and \([\text{Y}(L1^S)(\mu_2-F)(NO_3)_2](NO_3)_2\) complexes in 2 mM deuterated 2:1 chloroform:methanol at 295 K, upon excitation at 321 nm.

**Figure 13.** CD spectrum of CDCl3/CD3OD 2:1 v/v solution of the equimolar mixture of \([\text{Y}(L1^S)(NO_3)_2](NO_3)\) and \([\text{Nd}(L3)(NO_3)_2](NO_3)_2\) complexes generated after addition of 1 equiv (top) and 2 equiv (bottom) of NEt4F.

**Figure 14.** Top: CD spectrum of water solution of the equimolar mixture of \([\text{Nd}(L1^S)(NO_3)_2](NO_3)\) and \([\text{Dy}(L3)(NO_3)_2](NO_3)_2\) complexes. Bottom: CD spectrum of the same mixture after addition of 1 equiv of NEt4F. Label Dy denotes f–f transitions of the dysprosium(III) cation bound by the achiral L3 macrocycle, and the label Nd denotes f–f transitions of neodymium(III) bound by the chiral L1 macrocycle.

In another CD experiment a starting mixture of monomeric \([\text{Nd}(L1)(NO_3)_2](NO_3)\) and \([\text{Dy}(L3)(NO_3)_2](NO_3)\) was used. This mixture generated CD signals of the Nd(III) ion residing within the chiral macrocycle L1, but no CD signals due to Dy(III) ions residing within achiral macrocycle L3 were observed. After addition of 1 equiv of NEt4F, the Nd(III) signal changed due to the formation of fluoride-bridged dinuclear species, and a new weak signal corresponding to the f–f transitions of Dy(III) ion appeared due to chirality transfer (Figure 14). It is worth mentioning that the Nd(III) signals of the generated dinuclear species are very similar to those generated after addition of 1 equiv of fluoride in the previous experiment described above. Thus, the shape of the Nd(III) CD signal is analogous for the \([\text{Nd}(L1^S)\text{Dy}(L3)(\mu_2-F)_2(NO_3)_2]^2+\) and \([\text{Y}(L1^S)\text{Nd}(L3)(\mu_2-F)_2(NO_3)_2]^2+\) dinuclear...
species. This confirms that the macrocycles L1 and L3 assume the same direction of helical twist in these two different fluoride-bridged complexes. The similarity of these CD signals also indicates that the kind of hexaza-macrocycle does not influence much the crystal field parameters of the Nd(III).

**CONCLUSIONS**

Ln(III) complexes of hexaza-macrocycles L1–L3 tend to form dimers where two macrocyclic units are linked by two or three bridging fluoride anions. This contrasts the behavior of Ln(III) complexes with cyclen-based tetraaza-macrocycles where dimers are linked by single fluoride anions or mononuclear complexes with terminal fluoride are generated in reactions with fluoride salts. This difference reflects more open axial coordination spheres of the complexes of hexaza-macrocycles. Within these dimeric complexes the macrocyclic units L1–L3 are in a relatively close contact, and the steric interactions between them leads to sorting phenomena. Formation of the dinuclear fluoride-bridged complexes based on the chiral macrocycle L1 is accompanied by narcissistic sorting of macrocyclic units based on chirality (enantiomeric self-recognition). In the systems containing the mixture of Ln(III) complexes of two different macrocyclic ligands the formation of fluoride derivatives is influenced by matching of the shapes of the two macrocyclic units. Thus, the reactions of a mixture of complexes of macrocycle L1 and L2 or macrocycles L2 and L3 is accompanied by narcissistic sorting of macrocyclic units. On the other hand, in the case of the pair of macrocyclic complexes L1 and L3, the formation of fluoride-bridged dinuclear complexes is accompanied by social sorting of macrocyclic units. In this case the formation of mixed dimers is accompanied by chirality transfer from the chiral macrocycle L1 to achiral macrocycle L3. Steric interactions between macrocyclic units in heterodinuclear complexes of the type [Ln(L1)Ln(L3)(μ-F)2(NO3)2]2+ cause the macrocycle L3 to adopt a preferred direction of helical twist matching the helicity of the L1 unit. In turn, the direction of helical twist of macrocycle L1 is predetermined by the configuration at the chiral carbon atoms. This chirality transfer effect manifests itself in the appearance of CPL and CD signals corresponding to f−f transitions of Ln(III) ions bound by the achiral L3 unit.

**EXPERIMENTAL SECTION**

Details of structure determination and CPL measurements are provided in the Supporting Information.

**Synthesis of Mononuclear Complexes.** The Ln(III) complexes of macrocycles L1 and L3 have been obtained as reported previously.9,63,117 The [Ln(L2)2Cl2]2− (Ln = La, Ce, Eu, Dy) complexes were obtained in a similar manner as reported previously,9,63,85 as were new complexes of this type (Ln = Pr, Nd, Tb, and Y) as well as enantiomeric complexes [Ln(L2)2(NO3)2]2(H2O). 75.7 mg (0.1 mmol) of (Nd(L1)2(NO3)2]2(H2O) was suspended in 2 mL of methanol and mixed with the solution of 5.8 mg of KF (0.1 mmol) in 100 µL of methanol. The mixture was vigorously stirred for 2 h, filtered, and washed with methanol. Yield 43 mg, 59%. Anal. Calc. for C60H62Nd2N2O8: C, 57.05; H, 4.36; N, 15.15. Found: C, 56.58; H, 3.84; N, 15.06. NMR (CDCl3/CD2OD 2:1 v/v, 298 K, 500 MHz): δH 1.13, 8.89, 8.76, 7.44, 4.86, 3.64, 2.62, 2.02, 1.13, 0.89, 0.67, 0.27, −1.85. IR (KBr pellet cm−1): 3435, 3070, 2931, 2863, 1652, 1592, 1466, 1451, 1384, 1354, 1045, 1049, 823, 580.

**Synthesis of Dinuclear Complexes.** [Nd2(L1)2(μ-F)2(NO3)2]2+H2O. 76.5 mg (0.1 mmol) of [Eu(L1)2(NO3)2]2(H2O) was suspended in 3 mL of methanol and mixed with the solution of 5.8 mg of KF (0.1 mmol) in 100 µL of methanol. The mixture was vigorously stirred for 48 h, and the precipitate was filtered, washed with 1 mL of methanol, and dried in air. Yield 48 mg, 65%. Anal. Calc. for C68H54Nd2N3O12: C, 52.23; H, 3.46; N, 15.15. Found: C, 52.27; H, 3.17; N, 14.76. NMR (CDCl3/CD2OD 2:1 v/v, 298 K, 500 MHz): δH 1.13, 8.89, 8.76, 7.44, 4.86, 3.64, 2.62, 2.02, 1.13, 0.89, 0.67, 0.27, −1.85. IR (KBr pellet cm−1): 3435, 3070, 2931, 2863, 1652, 1592, 1466, 1451, 1384, 1212, 1111, 1045, 1049, 823, 580.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03034.
Crystallographic data and details of structure refinement; details of CPL measurements; Figures S1–S10 (molecular structures and NMR spectra) (PDF)

Accession Codes
CCDC 2112764–2112769 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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