

Article

A Highly Luminescent Chiral Tetrahedral Eu4L4(L')4 Cage: Chirality Induction, Chirality memory and Circularly Polarized Luminescence

Yanyan Zhou, Hongfeng Li, Tianyu Zhu, Ting Gao, and Pengfei Yan

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b07178 • Publication Date (Web): 20 Nov 2019 Downloaded from pubs.acs.org on November 20, 2019

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

2 3

4 5

6 7

8

9 10

11

12

13

14

15

16

17

18

19

20

21

22

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

A Highly Luminescent Chiral Tetrahedral Eu₄L₄(L['])₄ Cage: Chirality Induction, Chirality memory and Circularly Polarized Luminescence

Yanyan Zhou, Hongfeng Li,* Tianyu Zhu, Ting Gao and Pengfei Yan*

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education; School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China

ABSTRACT: Chiral lanthanide cages with circularly polarized luminescence (CPL) properties have found potential application in enantioselective guest recognition and sensing. However, it still remains a big challenge to develop simple and robust method for the diastereoselective assembly of homochiral lanthanide cage in view of the large lability of the Ln(III) ions. Herein, we report the first example of the formation of enantiopure lanthanide tetrahedral cage *via* chiral ancillary ligand induction strategy. One such [(Eu₄L₄)(R/S-BINAPO)₄] cage is assembled by four achiral C₃-symmeric tris- β -diketones [4,4',4"-tri(4,4,4-trifluoro-1,3-dioxobutyl)triphenylamine, L)] as faces, four Eu(III) ions as vertices, and four chiral R/S-bis(diphenylphosphoryl)-1,1'-binaphthyl (R/S-BINAPO) as ancillary ligands. X-ray crystallography, NMR and CD spectra confirm the formation of a pair of enantiopure chiral topological tetrahedral cages (Eu₄L₄)(R-BINAPO)₄ and (Eu₄L₄)(S-BINAPO)₄ ($\Delta\Delta\Delta\Delta$ -1 and $\Lambda\Lambda\Lambda\Lambda$ -1). As expected, the tetrahedral cages present strong CPL with the |g_{lum}| up to 0.20, while unexpectedly give the ultrahigh luminescent quantum yields (QYs) of up to 81%, a highest value reported in chiral Ln(III) complexes. More impressively, the chiral memory effect for lanthanide-based assembly is observed for the first time. The chirality of the original cage-1 framework is retained after the R/S-BINAPO being replaced by achiral bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO), and thus another pair of enantiopure Eu(III) tetrahedral cages $\Delta\Delta\Delta\Delta$ - and $\Lambda\Lambda\Lambda\Lambda$ -[(Eu₄L₄)(DPEPO)₄] ($\Delta\Delta\Delta\Delta$ -2 and $\Lambda\Lambda\Lambda\Lambda$ -2) are isolated. Encouragingly, cage-2 also presents impressive luminescence quantum yield (QYs = 68%) and intense CPL (|g_{lum}| = 0.10). This study offers a simple and low-cost synthesis strategy for the preparation of lanthanide cage with CPL properties.

Introduction

Chiral circularly polarized luminescence (CPL) materials have been attracting increasing attention in recent years for their potential applications in biological probes,¹ threedimensional (3D) displays,² optical storage,³ and chiral photoelectric devices.⁴ Because the existence of magnetic dipole transition, the lanthanide complexes show obviously higher luminescence dissymmetry factor glum (10those of fluorescence molecules,5 than ²-0.5) supramolecular aggregates,6 polymers,7 transition metal complexes (10⁻⁵-10⁻³).⁸ Since 1970s, the simple chiral mononuclear Ln(III) complexes are the most extensively studied CPL materials,9 and some of which have been developed as chiral probe10 and luminescent layers of OLED.11 In contrast with mononuclear system,12 the chiral dinuclear helicate¹³ and more sophistical polynuclear architectures such as chiral tetranuclear tetrahedron¹⁴ are much less explored for CPL investigation due to their difficulties in controlling the stereochemistry of the assemblies.

Metal-organic supramolecular cages with chirotopic cavities enabling encapsulation of guests have proved useful in stereoselective guest recognition,¹⁵ sensing,¹⁶ and as asymmetric reaction vessels.¹⁷ Supposing that the chiral supramolecular cage is rendered with CPL characteristic, it would undoubtedly extend their applications, especially in chiral sensing area. A general strategy for controlling the stereochemistry of the cage is the introduction of chiral elements,¹⁸ such as using enantiopure building blocks,¹⁹ chiral counterions,²⁰ chiral guests,²¹ or chiral ancillary ligand.²² However, the Ln(III) ions are very rarely selected as metal center of cage, because their variable coordination numbers (6–12), complicated and undefined coordination geometries make the control of the stereochemistry during the self-assembly process is rather challenging.²³ As reported by Sun, and Law that the slight structure changes on the spacers or the terminal chiral amines of the ditopic ligands, either cause the structural transformation from tetrahedron to helicate or cube, or the presence of diastereoselective breaking.^{14,24}

On the other hand, the large coordination numbers of Ln(III) ions (commonly 8–10) also offers the chance for the introduction of chiral ancillary ligand to regulate the stereochemistry of assemblies, which is rarely realized in 3d transition metal cages due to their limited coordination numbers (commonly 4-6).^{22,25} We infer that the introduction of chiral ancillary ligand with large steric hindrance would effectively control the diastereoselectivity in self-assembly process. In this context, a $[(Eu_4L_4)(R/S-BINAPO)_4]$ tetrahedron cage is synthesized by employing four achiral C₃-symmeric tris-βdiketones [4,4',4"-tri(4,4,4-trifluoro-1,3dioxobutyl)triphenylamine, L)] as faces, four Eu(III) ions as vertices, and four chiral R/S-bis(diphenylphosphoryl)-1,1'binaphthyl (R/S-BINAPO) as ancillary ligands. Single crystal X-ray crystallographic analyses show that two R/S-BINAPO enantiomers successfully induce diastereoselective self-assembly of a pair of enantiopure Eu(III) tetrahedral cages, $(Eu_4L_4)(R-BINAPO)_4$ and $(Eu_4L_4)(S-BINAPO)_4$ $(\Delta\Delta\Delta\Delta-\mathbf{1} \text{ and } \Lambda\Lambda\Lambda-\mathbf{1}).$ The photophysical experiment results show that the cage-1 present strong circularly polarized luminescence with the $|g_{lum}|$ up to 0.20, and the highest luminescent quantum yields (QYs = 81%) among the chiral lanthanide complexes reported so far.

As chiral luminescence materials, expensive chiral source is a key factor to hinder their widespread use in Environment future. Inspired by chirality-memory principle,²⁶ we examine the chiral memory effect of the cage-1 by employing an achiral bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) to replace the chiral R/S-BINAPO. Encouragingly, the configurations of the enantiopure (Eu₄L₄)(R-BINAPO)₄ and (Eu₄L₄)(S-BINAPO)₄ ($\Delta\Delta\Delta\Delta$ -1 and $\Lambda\Lambda\Lambda\Lambda$ -1) are preserved during the substitution process, and thus another pair of new enantiopure tetrahedral cages $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$ -[(Eu₄L₄)(DPEPO)₄] ($\Delta\Delta\Delta\Delta$ -2 and $\Lambda\Lambda\Lambda\Lambda$ -2) are isolated. CD and CPL experiments verify their optical activity despite the absence of chiral elements in two ligands. Two possible substitution pathways for the stereochemical memory are proposed by means of CD and a simple reaction kinetic experiments, which enable us to well control the enantiomer purity.

Scheme 1. Syntheses of the tetrahedral cages-1 and -2



Results and discussion

Synthesis and Characterization of Ligand and Tetrahedral Cage. The C₃-symmetric achiral tris- β diketone ligand [4,4',4"-tri(4,4,4-trifluoro-1,3dioxobutyl)triphenylamine, L)] is synthesized in two steps *via* a Friedel-Crafts acylation to afford the intermediate 4,4',4"-triacetyl triphenylamine, followed by a traditional Claisen condensation reaction to obtain the desired molecule (see Supporting Information for details). 'H NMR and ESI-TOF-MS confirm the formation and purity of the intermediate and ligand (Figures S1–S4).

The Ln(III) tetrahedral cages are obtained by stirring a 1:1:1 mixture of L, (R/S)-BINAPO and the corresponding Ln(III) salts in methanol at room temperature. ¹H, ³¹P, ¹⁹F NMR and DOSY NMR suggest the formation of a single species in solution. Due to the poor resolution of the ¹H NMR for Eu(III) complexes (Figure S5, S6), the isostructural Y(III) complexes, $[(Y_4L_4)(R/S-BINAPO)_4,$ cage-3] are chosen as substitute for ¹H NMR experiments (Figure S7–S10, COSY; NOESY). As shown in Figure 1b, the cage-3 show a single set of broadened but distinguishing signals. Compared with the two free ligands, the most of the signals from the tetrahedral cage undergo high-field shifts. Especially, three groups of resonances from tris-βdiketone are easier to be distinguished, which show limited broadening after the coordination with the metal. Moreover, there is no observation of new peaks attributed to Lindicating the high diastereopurity of the cages. ³¹P and ¹⁹F NMR spectra also indicate the formation of a single species, with only one sharp singlet peak observed in cage-1 and cage-3 (Figure S11–S14). Furthermore, ¹H NMR diffusion ordered spectroscopy (DOSY) of cage-1 and cage-3 show one diffusion band at a diffusion coefficient of D = 4.03×10^{-6} cm² s⁻¹ and 5.88×10^{-6} cm² s⁻¹, respectively, in line with the formation of a single species (Figure 1c, Figure S15, S16). The dynamic radii of the tetrahedron is calculated to be 32 Å with the Stokes-Einstein equation, which is in good agreement with that observed from the crystal structure of cage-1 (vide infra for structure analysis). High-resolution electrospray ionization mass spectrometry (ESI-TOF-MS) analyses further confirm the formation of tetrahedral supramolecular architecture with a formula of $(Ln_4L_4)(R/S-$ BINAPO)₄ (Figure S17–S20). The spectra show the

58 59

60

1

2

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23 24

25

26

27

28

29

30 31 32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

corresponding molecular ion peaks of the cages, and their isotopic patterns agreed well with the simulated isotopic distributions.



Figure 1. (a) ¹H NMR assignment of L and (R)-BINAPO. (b) ¹H NMR (400 MHz) spectra of free ligands L, (R)-BINAPO and their self-assembled yttrium complexes $(Y_4L_4)(R-BINAPO)_4$ and $(Y_4L_4)(S-BINAPO)_4$ ($\Delta\Delta\Delta\Delta-3$ and $\Lambda\Lambda\Lambda\Lambda-3$) in CDCl₃. (c) ¹H DOSY spectrum of $\Delta\Delta\Delta\Delta-3$ in CDCl₃. Asterisk denotes the solvent NMR peak.

X-ray Crystal Structure of Eu(III) Tetrahedral Cage. To better understand how chiral (R/S)-BINAPO induce achiral L to form diastereopure tetrahedral cage, the X-ray-quality crystals of $(Eu_4L_4)(R-BINAPO)_4$ and $(Eu_4L_4)(S-BINAPO)_4$ ($\Delta\Delta\Delta\Delta$ -1 and $\Lambda\Lambda\Lambda\Lambda$ -1) are grown from a THF-hexane solution. X-ray diffraction analyses reveal that $\Delta\Delta\Delta\Delta$ -1 and $\Lambda\Lambda\Lambda\Lambda$ -1 are the expected M_4L_4 tetrahedral structure (Figure 2a and 2b), and both crystallize in the chiral space group I_{222} , suggesting that chirality deriving from chiral R/S-BINAPO has been transferred successfully into the resulting solid structures. In cage-1, four europium ions site on the vertices, and four ligands span the faces. Interestingly, the triangle formed by its three Eu(III) centers is scalene, with the distances between each two metals centres being 13.158 Å, 14.846 Å and 15.394 Å, respectively. In one cage, each Eu centre is chelated by three β -diketonate units from three ligands and one BINAPO molecule, giving rise to a distorted triangular dodecahedron coordination geometry (Figure

S21). In (Eu_4L_4) (S-BINAPO)₄, each three β -diketonate units helically wrap about an Eu(III) centre in a left-hand propeller-like fashion, leading to a Λ configuration at each of the four vertices. In contrast, a Δ configuration around the metal center is observed in (Eu_4L_4) (R-BINAPO)₄.

We propose that the formation of homochiral $\Delta\Delta\Delta\Delta$ -1 and AAAA-1 enantiomers should attribute to the chiral induction of R/S-BINAPO and the mechanical coupling through the rigid ligands. In $\Lambda\Lambda\Lambda\Lambda$ -1, by viewing along the pseudo-C₃ symmetry axis direction of a tetrahedron (Figure 2c and 2d), one can observe that the O, P and C atoms in a S-BINAPO form a left-hand helical clamp, with the configuration being consistent with that observed in triple stranded helix around metal center. While the opposite case can be observed in $\Delta\Delta\Delta\Delta$ -1. From a geometric point of view, as two helixes move closer together by a head-to-head orientation, adopting the same helical conformations is energy favorable. Additionally, a plenty of intramolecular C-H···X interaction between the F, O atoms of L and H atoms of BINAPO are formed at each of its Eu(III) vertice (Figure S22). We suggest that these weak interactions play vital roles for inducing and stabilizing the resulting homochiral structure.



Figure 2. Crystallographic structures of (a) $(Eu_4L_4)(R-BINAPO)_4$ ($\Delta\Delta\Delta\Delta$ -1) and (b) $(Eu_4L_4)(S-BINAPO)_4$ ($\Lambda\Lambda\Lambda\Lambda$ -1). (c) Side view and (d) top view of the helical configuration of (S)-BINAPO.

On the other hand, in contrast to the most of homochiral 3d transition metal-based tetrahedra with well-defined T point symmetry,²⁷ $\Delta\Delta\Delta\Delta$ -1 and $\Lambda\Lambda\Lambda\Lambda$ -1 have highly twisted tetrahedral backbone that obviously deviate from T-symmetry. It is because of the large steric bulk of R/S-BINAPO that enforces the L losing C₃-symmetry. Notably, the twisted structure as well as the propeller-like conformation of the triphenylamine (TPA) units are

expected to effectively prevent luminescence quenching caused by intermolecular aggregation.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

Chiral optical properties. The UV-vis and CD spectra of $(Eu_4L_4)(R-BINAPO)_4$ and $(Eu_4L_4)(S-BINAPO)_4$ ($\Delta\Delta\Delta\Delta-1$ and $\Lambda\Lambda\Lambda\Lambda$ -1)in CHCl₃ are shown in Figure 3a. As expected, the enantiomers show the same absorbance curves and mirror-image CD signals. In the range of 220-450 nm, three well-resolved absorbance bands can be observed. The high energy bands in 220-275 nm range are attributed to the π - π ^{*} transition of chiral R/S-BINAPO, and show mirror-image Cotton effects at 243 nm (negative signal for $\Lambda\Lambda\Lambda\Lambda$ -1 and positive signal for $\Delta\Delta\Delta\Delta$ -1) and 261 nm (positive signal for $\Lambda\Lambda\Lambda\Lambda$ -1 and negative signal for $\Delta\Delta\Delta\Delta$ -1, respectively. The other two bands in the ranges of 280-350 nm and 350-450 nm are attributed to the characteristic absorbance of achiral tris-β-diketone ligand. The relatively intense absorbance at lower energy band are attributed to π - π * charge transfer (CT) transition from triphenylamine core to withdrawing β -diketone units. Moreover, a shoulder is observed at about 400 nm, an exciton coupling characteristics arising from the spatial proximity of three coordination β-diketone arms around one Eu(III) center.²⁸ Compared with the absorbance of free L (Figure S23), the band exhibits apparent hypsochromic shift with the maxima from 430 nm to 383 nm. It is reasonable that the higher degree twist of ligand wrapping the metal center reduce the conjugation of the π -skeleton. While the higher energy absorbance in 280-350 nm are complicated and exhibit several vibrational progressions with a spacing of $(5.9-6.7) \times 10^5$ cm⁻¹ (ring breathing feature), which should be attributed to π - π * transitions of the triphenylamine core and the intra-diketones.

In CD spectra, the achiral tris-*β*-diketone shows two large exciton couplets with the Davydov splitting of 40 nm and 25 nm, respectively, representing two Cotton effect splits of the 392 nm- and 316 nm-centered absorbance bands. This result indicates the chirality of R/S-BINAPO have been successfully transferred into the L, where the helical chirality is formed. In $(Eu_4L_4)(R-BINAPO)_4$, the two bands both show negative exciton couplets, corresponding to the Δ configuration around the Eu(III) ion; conversely, a positive exciton couplet associated with Λ configuration is observed for $(Eu_{4}L_{4})(S-BINAPO)_{4}$. These results accord with the general rule used for relating the sign of the exciton couplet with the absolute configuration of the metal centre for the family of octahedral tris(bidentate) complexes.²⁹ Although the application of this empirical rule to assign the absolute configuration of Ln(III) complexes are rare, several examples reported still prove its universality.30

The CPL and PL spectra of $(Eu_4L_4)(R-BINAPO)_4$ and $(Eu_4L_4)(S-BINAPO)_4$ in CHCl₃ are shown in Figure 3b. The enantiomers exhibit almost identical emission spectra, but show mirror image CPL spectra. The excitation spectra are obtained by monitoring the emission maxima of Eu(III) ion at 612 nm (Figure S24), which well match their absorption spectra (Figure S25). Upon excitation with the β -diketonate antennae moieties at 395 nm, the emission spectra of $(Eu_4L_4)(R-BINAPO)_4$ and $(Eu_4L_4)(S-BINAPO)_4$

show five characteristic emission bands of Eu(III) ion at 578, 592, 612, 650, and 700 nm, corresponding to ${}^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions, respectively. Under 365 nm UV light, the cages emit very strong red luminescence in CHCl₃ (Figure 3b, insert). The Eu(III) center luminescence quantum yields $\Phi_{overall}$ are measured to be 81% (Figure S26, S27), which represent the highest value for chiral Ln-based complexes in solution. With the broad excitation window in the visible region up to 450 nm, the cage even emits bright red light under natural illumination.



Figure 3. (a) UV-visible absorption (lower curve, right axis) and CD spectra (upper curves, left axis) of $(Eu_4L_4)(R-BINAPO)_4$ ($\Delta\Delta\Delta\Delta$ -1) (blue lines) and $(Eu_4L_4)(S-BINAPO)_4$ ($\Lambda\Lambda\Lambda\Lambda$ -1) (red lines) in CHCl₃ (2.5 × 10⁻⁶ M). (b) Total luminescence (lower curve, right axis) and CPL spectra (upper curves, left axis) of $\Delta\Delta\Delta\Delta$ -1 (blue lines) and $\Lambda\Lambda\Lambda\Lambda$ -1 (red lines) in CHCl₃ (λ_{ex} = 395 nm, 2.5 × 10⁻⁶ M).

The CPL spectra show two relatively intense emitting signals at 592 nm and 612 nm, which are attributed to the ${}^5D_o \rightarrow {}^7F_1$ magnetic-dipole transition and ${}^5D_o \rightarrow {}^7F_2$ electronic-dipole transition, respectively. Generally, the magnetic dipole transition often shows particularly large circular polarization. The degree of the CPL is assessed in terms of the luminescent dissymmetry factor, g_{lum} . Herein, $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R represent the left and right polarized emission intensities, respectively (with $-2 \leq g_{lum} \leq 2$). The $|g_{lum}|$ values for ${}^5D_o \rightarrow {}^7F_1$ transitions of (Eu₄L₄)(R-BINAPO)₄ and (Eu₄L₄)(S-BINAPO)₄ are found to be 0.20, which are comparable to those of the reported Eu(III) complexes with chiral 2-hydroxyisophthalamide-, 1-hydroxy-2-pyridinone-, pyridyl diamide-, and DOTA-based ligands.³¹ In (Eu₄L₄)(R-BINAPO)₄, a negative CPL

signal at ${}^{5}D_{o} \rightarrow {}^{7}F_{2}$ transition and a positive CPL signal at ${}^{5}D_{o} \rightarrow {}^{7}F_{1}$ transition are observed, while the (Eu₄L₄)(S-BINAPO)₄ gives the mirror-image signals. The spectra signatures are in analogy with that of the exciton coupling in CD spectra. Therefore, it is suggested that the CPL spectral information can relate with the absolute configuration of lanthanide complexes, although the corresponding reports are rare.³²

Stereochemical Memory of the Cage. In consideration of the rigid of the ligand and the strong mechanical coupling usually existing in multinuclear metals framework,³³ we infer that the cage Ln_4L_4 could process and conserve the original information first introduced by chiral R/S-BINAPO after its replacement. Herein, we employ the achiral bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) to

replace the chiral R/S-BINAPO for examining the stereochemistry memory effect of the Ln-cage. In view of the similar bidentate structures, the coordination abilities for two PO ancillary ligands are probably the same or differ slightly with each other. Thus, the equivalent ratios of DPEPO to BINAPO for achieving the entire displacement is firstly studied. The progress of the reaction is monitored by CD spectra. Upon the addition of 4 equivalent of DPEPO to a solution of cage-1 (6×10^{-6} M in CHCl₃), the CD intensity shows a 16% drop after 48 h of reaction at 25 °C (Figure 4a). With further addition of DPEPO by each 4 equivalent (time interval 48 h), the decreased tendency gradually slow down, until the CD values tend to be constant after 32 equivalent addition (Figure 4b), suggesting the completion of the majority of the substitution.



Figure 4. (a) CD spectra of cage-1 and (b) their intensities at 368 nm with the addition of different equiv of DPEPO in CHCl₃ (cage-1, 6.0 × 10⁻⁶ M). (c) CD spectra of cage-1 and (d) their intensities at 368 nm with reaction time in the presence of 32 equiv of DPEPO in CHCl₃ (cage-1, 6.0 × 10⁻⁶ M). (e) ¹H NMR spectra of $(Y_4L_4)(R-BINAPO)_4$ ($\Delta\Delta\Delta\Delta$ -3) substituted by 32 equiv of DPEPO at different reaction times. (f) ³¹P NMR spectra of the filtrate of $(Y_4L_4)(DPEPO)_4$ ($\Delta\Delta\Delta\Delta$ -4) prepared from $\Delta\Delta\Delta\Delta$ -3 via the two (Sub.2) and three times (Sub.3) substitutions.

To monitor the substitution rate, the CD intensity variations (at 368 nm) with reaction time are monitored in the presence of 32 equivalent of DPEPO (Figure 4c). As shown in Figure 4d, the $\Delta \varepsilon$ shows a gradual decrease with the reaction time until reaching a plateau after stirring for 36 h, indicating the completion of substitution. The luminescence intensities variations (at 612 nm) with the time show a similar tendency as that observed in CD measurement (Figure S28).

This process is also monitored by the employment of ¹H NMR spectroscopy. To eliminate the interference of the excess DPEPO on NMR measurement, at the end of each reaction time interval (12 h), the partially substituted species is isolated as precipitate by the addition of excess n-hexane to its CHCl₃ solution. As shown in Figure 4e, during the course of the reaction, ¹H NMR spectra show temporary desymmetrization and broaden, eventually

converging to a spectrum consistent with the racemic $(Y_4L_4)(DPEPO)_4$ (cage-4) after 48 h of reaction (Figure S29).

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35 36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

To insure the complete substitution for R/S-BINAPO, the firstly substituted and isolated product is re-reacted twice with 32 equivalent DPEPO. ³¹P NMR spectrum of the filtrate of the second times substituted product shows a trace of free R-BINAPO signal at 28.8 ppm (Figure 4f, sub.2), indicating the firstly substituted product with a trace of R-BINAPO ligating on the cage. However, the signal of R-BINAPO disappears after the third times repetition (Figure 4f, sub.3), which indicates the pure cage-2, $(Eu_4L_4)(DPEPO)_4$ are obtained. The purity of the cages-2, $(Eu_{4}L_{4})(DPEPO)_{4}$ and cage-4, $(Y_{4}L_{4})(DPEPO)_{4}$ are further confirmed by NMR and ESI-MS measurements (Figure S₃₀–S₄₅). Notably, the CD intensities of three times substitution products are almost the same (Figure S46), which indicates the optical activity originating from the tetrahedral backbone is well preserved, although a large amount of achiral DPEPO exist in solution.

To rule out the possibility that the optical activity observed in this system arising from the trace amount of R/S-BINAPO in solution, we perform a control experiment. The cage-2 prepared from the assemble of L and Ln(III) ions in the presence of 32 equivalent of DPEPO and 4 equivalent of R-BINAPO or the stirring of a solution of racemic cage-2 in the presence of 4 equivalent of R-BINAPO and 28 equivalent DPEPO for 48 h, both show negligible CD signals (Figure S47).



Figure 5. (a) UV-visible absorption (lower curve, right axis) and CD spectra (upper curves, left axis) of $\Delta\Delta\Delta\Delta$ -(Eu₄L₄)(DPEPO)₄ ($\Delta\Delta\Delta\Delta$ -**2**, blue lines) and $\Lambda\Lambda\Lambda\Lambda$ -(Eu₄L₄)(DPEPO)₄ ($\Lambda\Lambda\Lambda\Lambda$ -**2**, red lines) in CHCl₃ (2.5 × 10⁻⁶ M). (b) Total luminescence (lower curve, right axis) and CPL spectra (upper curves, left axis) of $\Delta\Delta\Delta\Delta$ -**2** (blue lines)

and $\Lambda\Lambda\Lambda\Lambda$ -2 (red lines) in CHCl₃ ($\lambda_{ex} = 395$ nm, 2.5×10^{-6} M).

The CD spectra of the cage-2 prepared from $\Delta\Delta\Delta\Delta$ -/AAAA-1 show mirror-image CD signals and similar spectral signatures as observed in cage-1. The same exciton coupling signs suggest the configuration of cage-1 is retained during the exchange process, and another pair of enantiomeric tetrahedral cages $\Delta\Delta\Delta\Delta$ - and $\Lambda\Lambda\Lambda\Lambda$ - $[(Eu_4L_4)(DPEPO)_4]$ ($\Delta\Delta\Delta\Delta-2$ and $\Lambda\Lambda\Lambda\Lambda-2$) are obtained. Compared with the CD spectra of the cage-1, the magnitude of molar ECD ($\Delta \epsilon$) of three exciton coupling drop about 55%. We suggest that this drop should relate to the changes of the coordination environment around Ln(III) ion. From the optimized structure (Figure S48), by calculations using LUMPAC with a Sparkle/PM6 model,34 we can observe that the relatively flexible structure of DPEPO release the tension of the highly twisted tetrahedral backbone caused by BINAPO. The distances between two metal centers in a triangle plane change from 13.158 Å, 14.846 Å and 15.394 Å in cage-1 to 13.493 Å, 14.895 Å and 14.908 Å in cage-2, a less deviatation from T symmetry. Notably, the CD signals arising from achiral DPEPO are observed at low wavelength range (230-280 nm), which indicates the chirality from the cage has transferred to the DPEPO. In other word, a chiral cage comprised of achiral elements is successfully constructed after a successive chiral induction and exchange.

The cage-2 also display mirror-image CPL signals and the similar spectral signatures as that in cage-1, in line with the expected retention of the configuration around the Eu(III) ions. The $|g_{lum}|$ values for ${}^5D_o \rightarrow {}^7F_1$ transitions of cage-2 are found to be 0.11, which is about the half of the value of cage-1. The cage-2 also show bright red emission under UV light and naked-eye visible luminescence under room light. The luminescence quantum yields $\Phi_{overall}$ are measured to be 68% (Figure S49, 50).

Finally, the stability of the cage-1 and cage-2 in different polar solvents and their abilities to resists hydrolysis are investigated in view of their potential applications on bioanalytical assays. In CHCl₃, THF and methanol, the optical activity of the cages did not degrade after staying for 7 days at room temperature (Figure S₅₁–S₅₃). During this period, there were no new sets of resonances relating to L and/or free PO ligand present in ¹H NMR of corresponding Y-cages (Figure S54–S59). These observations prove that the structures of the cages are stable in these solvents. While, in DMSO, the optical activity disappeared (Figure S6o), and the signals from the free BINAPO and DPEPO can be observed in ¹H NMR (Figure S61, S62). This can be explained from the strong coordination ability of DMSO, where PO ligands are replaced. In methanol/ H_2O (v:v = 99:1), the cages are also relatively stable, as indicated by their CD and ¹H NMR spectra (Figure S63–S65). Upon the addition of HCl and NaOH aqueous solution, the CD intensities initially show slightly drop, then a gradual decrease (Figure S66, S67), which are attributed to the part disruption of the cages, as confirmed by the observation of free L and PO ligands in ¹H NMR spectra (Figure S68-S71).

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

25 26

31 32

38

39 40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

These results indicate that the two cages enable to resists hydrolysis in relatively mild acidity and alkalinity conditions. However, the excess addition of acid or base, the irreversible hydrolysis of the free Ln(III) ions into hydroxides and the protonation of the L²⁻ will happen.

Mechanism of Chirality Memory. The CD and CPL measurement results reveal that the substitution process is stereoselective. We infer the transformation from cage-1 to cage-2 should proceed through two possible pathway: (1) association pathway, where the formation of activated complex that one metal centre is ligated with a BINAPO and a DPEPO is reasonable by expanding the coordination numbers of Ln ions. In this case, the dissociation of BINAPO will not lead to the inversion of configuration on the vertices; (2) dissociation pathway, where the substitution proceed following the dissociation of BINAPO from one and/or more vertices. The two proposed pathways are shown in Scheme 2.

The existence of dissociation pathway can be verified from the following concentration and temperature dependence experiments of the CD intensities. In the relatively higher concentration ranges (2.5 µM-1.0 mM), the molar ECDs ($\Delta \epsilon$) of (Eu₄L₄)(S-BINAPO)₄ remain constant, but at much lower concentration, 0.6 µM and 1.0 μ M, the $\Delta \epsilon$ have a 16.3% and 9.8% drops, respectively (Figure 6a, 6b). In the substitution experiment, a similar tendency is also observed (Figure 6c, 6d). Moreover, the substitution process also show temperature dependence. In temperature range of 10–30 °C, the $\Delta \varepsilon$ values tend to constant after 48 h of reaction (Figure S72–S74, Figure 6f). In contrast, the CD intensities gradually decrease until reaching to zero after reaction for 148 h at 40 °C (Figure 6e). These results are consistent with the suggested dissociation pathway, since the dissociative degree would be enhanced following with the decrease of the concentration and the increase of temperature. Notably, the $\Delta \varepsilon$ curves with reaction times are well overlapped at 10-30 °C ranges.

Scheme 2. Schematic representation of the two parallel pathways operating during the transformation of $\Delta\Delta\Delta\Delta$ -1 into $\Delta\Delta\Delta\Delta$ -2.



In the proposed dissociation pathway, there are four possible species in solution. We suggest the racemization of the cage at relatively dilute solution and the higher temperature should originate from the presence of a completed dissociation species IV, "naked cake", where the stereochemistry control from chiral R/S-BINAPO will disappear. For the other species I-III, the configuration of the cage would be maintained during the substitution process, because the partial chelation of chiral units will induce all the vertices to adopt the same helical handedness due to the strong mechanical coupling between the metal centers.35 On the base of the concentration and temperature dependence results, it can be concluded that the high fidelity stereochemical memory could be realized as the concentration of $[cage-1] \ge 0.25 \,\mu\text{M}$ and reaction temperature $T \le 30$ °C. However, it is a pity that the efforts for obtaining the *ee* values of $\Delta\Delta\Delta\Delta$ -2 and

ΛΛΛΛ-**2** by employing the chiral NMR chemical shift agents and chiral HPLC technologies are unsuccessful.³⁶

To gain further insight into the substitution mechanism, we perform a simple kinetic analysis for substitution process by monitoring the amounts of free BINAPO in solution by HPLC (Figure S75). In the temperature range of 10–40 °C, the fitting curves of the reaction time with the concentration of BINAPO neither well match the first-order kinetic nor the second-order reaction kinetic ($R^2 < 0.99$, Figure S76–S79). It indicates that the substitution process probably involve the both reaction kinetics simultaneously.

In dissociation pathway, the substitution process should obey first-order reaction kinetics as the dissociation of BINAPO from the cage-1 should be the rate-determining step. On the other hand, in association pathway the formation of transition state should be the rate-

estimated.

determining step, which can be described using secondorder reaction kinetics. With these analyses, we suggest that the two proposal pathways should coexist in the substitution process, and the each probably represents two poles of a continuum of possibilities in practice. With the

(a)

Δε (M⁻¹ cm⁻¹)

(b)

cm-1)

ž

S₄), the following thermodynamic parameters, $\Delta_r G = \theta m =$ 19.4 kJ mol⁻¹, $\Delta_r H\theta m = 11.9$ kJ mol⁻¹ and $\Delta_r S\theta m = -22.6$ J mol⁻¹ K-1 relating to the substitution process at 20 °C are

calculated apparent equilibrium constant K⁰ (Equation S1-(e) (C) 200 300 300 40 °C 150 150 100 cm_ 'm 0 Ē ž 132 h 0 -150 ∛ -150 Δε 12 h -100 -300 0.6 µM 0.6 µM -300 1.0 mM 1.0 mM 0 h -200 410 320 350 380 410 320 350 380 320 350 380 410 Wavelength (nm) Wavelength (nm) Wavelength (nm) (f) (d) -400 -175 -400 ○ 10 °C □ 20 °C -300 △ 30 °C cm_1 -350 -150 ່ຮູ 40 °C -200 ר_ע ענ (ע קי 125 μ_ Ψ) 3∇ -100 8880000000 -300 -250 -100 40 120 160 6x10-7 10-6 10-5 10-4 10-3 0 80 6x10⁻⁷ 10-6 10-5 10-4 10-3 c (mol/L) c (mol/L) Time (h)

Figure 6. (a) CD spectra of $(Eu_4L_4)(S-BINAPO)_4$ ($\Lambda\Lambda\Lambda\Lambda$ -1) and (b) their intensities at 368 nm in concentrations of 0.6 μ M– 1.0 mM in CHCl₂. (c) CD spectra of (Eu_4L_4) (S-BINAPO)₄ ($\Lambda\Lambda\Lambda\Lambda$ -1) and (b) their intensities at 368 nm in concentrations of 0.6 μ M-1.0 mM in the presence of 32 equiv of DPEPO after stirring 48 h in CHCl₃. (e) CD spectra of (Eu₄L₄)(S-BINAPO)₄ $(\Lambda\Lambda\Lambda\Lambda-1)$ with 32 equiv of DPEPO with different reaction time (T = 40 °C, cage-1, 2.5 μ M). (f) The plots of the CD intensity decay at 368 nm with reaction time under different reaction temperatures.

Ultrahigh Luminescence Quantum Yields Analyses. As excellent CPL materials, the high luminescence quantum yield (Φ_{tot}) is another important parameter for estimating the performance of the materials. Absolute luminescence quantum yields of the cage-1 and cage-2 in CHCl₃ are measured to be 81% and 68%, respectively. These ultrahigh luminescence quantum yields are rare in lanthanide materials.

We propose that the high luminescence quantum yields of the complexes should benefit from (1) effective sensitization ability of β -diketonate moieties on Eu(III) ions luminescence; (2) effective suppression of the nonradiative transition via vibrational relaxation in the complexes due to the introduction of PO ancillary ligands, which exclude the coordinated solvent molecules from the primary coordination sphere of the metal ions and strength the rigidity of the tetrahedral skeleton.

Table 1. Radiative (k_r) and nonradiative (k_{nr}) decay rates, observed luminescence lifetime of Eu³⁺ (τ_{obs}) , intrinsic quantum yield (Φ_{Ln}), sensitization efficiency (η_{sens}), quantum yield of Eu³⁺ (Φ_{Eu}), quantum yield of ligands (Φ_L) and overall quantum yield ($\Phi_{overall}$). Error in τ_{obs} : ±0.05 ms; 10% relative error in the other values; λ_{ex} = 395 nm. g_{lum} values for ${}^{5}D_{o} \rightarrow {}^{7}F_{I}$ of Eu³⁺ ion.

Cages	k _r (s ⁻¹)	k _{nr} (s ⁻¹)	τ _{obs} (μs)	Φ _{Ln} (%)	η _{sens} (%)	Φ _{overall} (%)	$g_{ium} {}^5D_0 \rightarrow {}^7F_J (J = 0, 1, 2, 3, 4)$				
							J = 0	J = 1	J = 2	J = 3	J = 4
ΔΔΔΔ- 1	1506	274	562	84.6	96.1	81.3	0.007	0.202	-0.009	0.021	0.050
////- 1	1509	270	563	84.8	95.6	81.1	-0.007	-0.204	0.008	-0.022	-0.049
۵۵۵۵- 2	1283	509	558	71.6	95.3	68.2	0.009	0.113	-0.002	0.024	0.021
^^^- 2	1282	511	558	71.5	95.2	68.1	-0.009	-0.113	0.002	-0.024	-0.021

In order to clarify theses effects, we have estimated sensitization efficiency (η_{sens}), and radiative (k_r), nonradiative (k_{nr}) rate constants of the complexes by using the following equations:

$$\Phi_{overall} = \eta_{sen} \Phi_{Ln} \qquad (1)$$

$$\Phi_{Ln} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}}$$
(2)
$$k_r = \frac{1}{\tau_{rad}} = A_{MD, 0} n^3 \left(\frac{I_{tot}}{I_{MD}}\right)$$
(3)

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

As shown in equation 1, the luminescence quantum yield (Φ_{overall}) is determined by the efficiency of the energy transfer (η_{sen}) and by the intrinsic quantum yield (Φ_{Ln}) of the lanthanide luminescence.

The intrinsic quantum yields of europium luminescence could be estimated by using the equation 2, after the calculation of the radiative lifetime (τ_{rad}) from equation 3. Where $A_{MD,o} = 14.65 \text{ s}^{-1}$ is the spontaneous emission probability of the magnetic dipole ${}^5D_o \rightarrow {}^7F_1$ transition, *n* is the refractive index of the solution. I_{tot} is the total integrated emission of the ${}^5D_o \rightarrow {}^7F_1$ transitions, and I_{MD} is the integrated emission of the ${}^5D_o \rightarrow {}^7F_1$ transition. The observed lifetimes (τ_{obs}) are determined by monitoring the emission decay curves within the ${}^5D_o \rightarrow {}^7F_2$ transition at 612 nm (Figure S8o–S83).With the calculated radiative lifetimes (τ_{rad}) and observed lifetimes, the intrinsic quantum yields (Φ_{Ln}) are found to be 84% and 71% for cage-1 and cage-2.

According to equation 2, the intrinsic quantum yield is the result of radiative transition (k_r) competes with nonradiative transition (k_{nr}) processes. The corresponding parameters are summarized in Table 2. Compared with the cage-2, the cage-1 have the higher radiative rate constants and the lower nonradiative rate constants. Generally, the reduction of the geometrical symmetry of the coordination structure will leads to a larger radiative rate constant (k_r) .³⁷ Coordination geometry calculated by SHAPE 2.1 software show that the cage-1 has the lower symmetrical triangular dodecahedral structure (8-TDH, D_{2d}) than the square antiprismatic structure (8-SAP) for cage-2. Moreover, the lower k_{nr} for cage-1 can be rationalized by their higher degree twist backbone, the resulting rigidity well suppress energy loss via vibrational relaxation. Additionally, the efficiency of energy transfer for two complexes are about the same, up to 95%. Therefore, the higher luminescence quantum yields of the cages should ascribe to their relatively high intrinsic quantum yield and energy transfer efficiency.

Conclusion

In summary, a pair of enantiopure tetrahedral cage $[(Eu_4L_4)(R/S-BINAPO)_4]$ with excellent circularly polarized properties luminescence (CPL) are successfully synthesized. We, herein, report the first example of employing the chiral ancillary ligand to control the stereochemistry of lanthanide tetrahedron. X-ray crystallographic analysis reveals that the configuration of R/S-BINAPO relate to the homochiral configuration of the cage, and determining the exciton coupling signatures of the CD spectra and the Eu(III) center's CPL signs. The R-BINAPO induces the formation of a right-handed P helical homochiral cage, $\Delta\Delta\Delta\Delta$ -1, and a negative exciton coupling of CD signal and a positive CPL signal at ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition. The luminescence measurements show that the cage-1 present high circularly polarized luminescence with the $|g_{lum}|$ up to 0.20, and a highest value of luminescent quantum yields (QYs = 81%) that reported in chiral lanthanide materials.

On the other hand, we also report the first example of the chiral memory effect within the lanthanide assemblies. The chirality of cage-1 deriving from chiral ancillary ligands can be retained *via* the substitution with an achiral analogue. The mechanism analyses reveal that the stereoselective substitution process is high fidelity as the concentration [cage-1] $\ge 0.25 \,\mu$ M and reaction temperature T $\le 30 \,^{\circ}$ C, because the racemizing pathway arising from the complete dissociation of four ancillary ligands can be excluded or ignored on this condition. Encouragingly, cage-2 also present impressive luminescence quantum yield (QYs = 68%) and modest luminescence dissymmetry factors ($|g_{lum}| = 0.10$). All in all, this work provides a simple and low-cost synthesis strategy for fabricating chiral lanthanide cage with excellent CPL properties.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, supporting figures and tables, and X-ray crystallographic data for $[(Eu_4L_4)(R/S-BINAPO)_4]$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as entries CCDC 1935644 and 1936609.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lihongfeng@hlju.edu.cn *E-mail: Yanpf@vip.sina.com

ORCID

Hongfeng Li: 0000-0003-4646-0515

Pengfei Yan: 0000-0002-5124-1707

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work is financially supported by the National Natural Science Foundation of China (Nos. 51872077 & 51773054). We also thank the Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, P. R. China, for supporting this work. The authors thanks Prof. Xin B.-F. for helpful discussions on mechanism of chirality memory, and thanks Prof. Mao, G.-J. for assistance with NMR measurements.

REFERENCES

(1) (a) Zinna, F.; Di Bari, L. Lanthanide Circularly Polarized Luminescence: Bases and Applications, *Chirality*, **2015**, *27*, 1–13. (b) Shuvaev, S.; Fox, M. A.; Parker, D. Monitoring of the ADP/ATP Ratio by Induced Circularly Polarised Europium Luminescence, *Angew. Chem. Int. Ed.* **2018**, 57, 1–6.

(2) Lim, D.-Y. Potential application of spintronic light-emitting diode to binocular vision for three-dimensional display technology, *J. Korean Phys. Soc.* **2006**, *49*, S505–S508.

(3) Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. Dynamic Control and Amplification of Molecular Chirality by Circular Polarized Light, *Science*, **1996**, *273*, 1686–1688.

(4) (a) Zinna, F.; Voci, S.; Arrico L.; Brun, E.; Homberg, A.; Bouffier, L.; Funaioli, T.; Lacour, J.; Sojic, N.; Di Bari, L. Circularly-Polarized Electrochemiluminescence from a Chiral Bispyrene Organic Macrocycle, *Angew. Chem. Int. Ed.* **2019**, *58*, 6952–6956. (b) Li, M.; Li, S.-H.; Zhang, D.; Cai, M.; Duan, L.; Fung, M.-K.; Chen, C.-F. Stable Enantiomers Displaying Thermally Activated Delayed Fluorescence: Efficient OLEDs with Circularly Polarized Electroluminescence, *Angew. Chem. Int. Ed.* **2018**, *57*, 2889–2893.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

(5) (a) Feuillastre, S.; Pauton, M.; Gao, L.; Desmarchelier, A.; Riives, A. J.; Prim, D.; Tondelier, D.; Geffroy, B.; Muller, G.; Clavier, G.; Pieters, G. Design and Synthesis of New Circularly Polarized Thermally Activated Delayed Fluorescence Emitters, *J. Am. Chem. Soc.* **2016**, *13*8, 3990–3993. (b) Cruz, C. M.; Castro-Fernández, S.; Maçôas, E.; Cuerva, J. M.; Campaña, A. G. Undecabenzo[7]superhelicene: A Helical Nanographene Ribbon as a Circularly Polarized Luminescence Emitter, *Angew. Chem. Int. Ed.* **2018**, 57, 14782–14786.

(6) (a) Jiang, H.; Jiang, Y.; Han, J.; Zhang, L.; Liu, M. Helical Nanostructures: Chirality Transfer and a Photodriven Transformation from Superhelix to Nanokebab, *Angew. Chem. Int. Ed.* **2019**, *58*, 785–790. (b) Yang, D.; Duan, P.; Zhang, L.; Liu, M. Chirality and Energy Transfer Amplified Circularly Polarized Luminescence in Composite Nanohelix, *Nature Commun.* **2017**, *8*, 15727.

(7) (a) San Jose, B. A.; Yan, J.; Akagi, K. Dynamic Switching of the Circularly Polarized Luminescence of Disubstituted Polyacetylene by Selective Transmission through a Thermotropic Chiral Nematic Liquid Crystal, *Angew. Chem. Int. Ed.* **2014**, *53*, 10641–10644. (b) San Jose, B. A.; Matsushita, S.; Akagi, K. Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on Disubstituted Polyacetylene Derivatives That Exhibit High Dissymmetry Factors in Circularly Polarized Luminescence, *J. Am. Chem. Soc.* **2012**, *134*, 19795–19807.

(8) (a) Hellou, N.; Srebro-Hooper, M.; Favereau, L.; Zinna, F.; Caytan, E.; Toupet, L.; Dorcet, V.; Jean, M.; Vanthuyne, N.; Williams, J. A. G.; Di Bari, L.; Autschbach, J.; Crassous, J. Enantiopure Cycloiridiated Complexes Bearing a Pentahelicenic N-Heterocyclic Carbene and Displaying Long-Lived Circularly Polarized Phosphorescence, *Angew. Chem. Int. Ed.* **2017**, *56*, 8236– 8239. (b) Aoki, R.; Toyoda, R.; Kögel, J. F.; Sakamoto, R.; Kumar, J.; Kitagawa, Y.; Harano, K.; Kawai, T.; Nishihara, H. Bis(dipyrrinato)zinc(II) Complex Chiroptical Wires: Exfoliation into Single Strands and Intensification of Circularly Polarized Luminescence, *J. Am. Chem. Soc.* **2017**, *139*, 16024–16027.

(9) (a) Riehl, J. P.; Muller, G. Circularly Polarized Luminescence Spectroscopy From Lanthanide Systems. Handbook on the Physics and Chemistry of Rare Earths Elsevier: Amsterdam **2005**, Vol.34, Chapter 220, pp 289–357. (b) Lunkley, J. L.; Shirotani, D.; Yamanari, K.; Kaizaki, S. Muller, G. Extraordinary Circularly Polarized Luminescence Activity Exhibited by Cesium Tetrakis(3heptafluoro-butylryl-(+)-camphorato) Eu(III) Complexes in EtOH and CHCl₃ Solutions, *J. Am. Chem. Soc.* **2008**, *1*30, 13814–13815. (c) Dai, L.; Lo, W.-S.; Coates, I. D.; Pal, R.; Law, G.-L. New Class of Bright and Highly Stable Chiral Cyclen Europium Complexes for Circularly Polarized Luminescence Applications, *Inorg. Chem.* **2016**, *55*, 9065–9070.

(10) (a) Carr, R.; Evans, N. H.; Parker, D. Lanthanide Complexes as Chiral Probes Exploiting Circularly Polarized Luminescence, *Chem. Soc. Rev.* 2012, *41*, 7673–7686. (b) Shuvaev, S.; Suturina, E. A.; Mason, K.; Parker, D. Chiral Probes for α₁-AGP Reporting by Species-specific Induced Circularly Polarised Luminescence, *Chem. Sci.* 2018, *9*, 2996–3003.

(11) (a) Zinna, F.; Giovanella, U.; Di Bari, L. Highly Circularly Polarized Electroluminescence from a Chiral Europium Complex, *Adv. Mater.* 2015, 27, 1791–1795. (b) Zinna, F.; Pasini, M.; Galeotti, F.; Botta, C.; Di Bari, L.; Giovanella, U. Design of Lanthanide-Based OLEDs with Remarkable Circularly Polarized Electroluminescence, *Adv. Funct. Mater.* 2017, 27, 1603719.

(12) (a) Byrne, J. P.; Kitchen, J. A.; Gunnlaugsson, T. The Btp
[2,6-bis(1,2,3-triazol-4-yl)pyridine] Binding Motif: A New
Versatile Terdentate Ligand for Supramolecular and Coordination
Chemistry, *Chem. Soc. Rev.* 2014, *4*3, 5302–5325. (b) Barry, D. E.;

Caffrey, D. F.; Gunnlaugsson, T. Lanthanide-directed Synthesis of Luminescent Self-assembly Supramolecular Structures and Mechanically Bonded Systems from Acyclic Coordinating Organic Ligands, *Chem. Soc. Rev.* **2016**, *45*, 3244–3274. (c) Kitchen, J. A.; Barry, D. E.; Mercs, L.; Albrecht, M.; Peacock, R. D.; Gunnlaugsson, T. Circularly Polarized Lanthanide Luminescence from Langmuir–Blodgett Films Formed from Optically Active and Amphiphilic Eu^{III–}Based Self-Assembly Complexes, *Angew. Chem. Int. Ed.* **2012**, *51*, 704–708. (d) Shuvaev, S.; Starck, M.; Parker, D. Responsive, Water-Soluble Europium(III) Luminescent Probes, *Chem. Eur. J.* **2017**, *23*, 9974–9989.

(13) Stomeo, F.; Lincheneau, C.; Leonard, J. P.; O'Brien, J. E.; Peacock, R. D.; McCoy, C. P.; Gunnlaugsson, T. Metal-Directed Synthesis of Enantiomerially Pure Dimetallic Lanthanide Luminescent Triple-Stranded Helicates, *J. Am. Chem. Soc.* 2009, *131*, 9636–9637.

(14) Yeung, C.-T.; Yim, K.-H.; Wong, H.-Y.; Pal, R.; Lo, W.-S.; Yan, S.-C.; Wong, M. Y.-M.; Yufit, D.; Smiles, D. E.; McCormick, L. J.; Teat, S. J.; Shuh, D. K.; Wong, W.-T.; Law, G.-L. Chiral Transcription in Self-Assembled Tetrahedral Eu_4L_6 Chiral Cages Displaying Sizable Circularly Polarized Luminescence, *Nature Commun.* 2017, *8*, 1128.

(15) (a) Xuan, W.; Zhang, M.; Liu, Y.; Chen, Z.; Cui, Y. A Chiral Quadruple-Stranded Helicate Cage for Enantioselective Recognition and Separation, *J. Am. Chem. Soc.* **2012**, *134*, 6904–6907. (b) Hou, Y.-J.; Wu, K.; Wei, Z.-W.; Li, K.; Lu, Y.L.; Zhu, C.-Y.; Wang, J.-S.; Pan, M.; Jiang, J.-J.; Li, G.Q.; Su, C.-Y. Design and Enantioresolution of Homochiral Fe(II)–Pd(II) Coordination Cages from Stereolabile Metalloligands: Stereochemical Stability and Enantioselective Separation, *J. Am. Chem. Soc.* **2018**, *140*, 18183–18191. (c) Wu, K.; Li, K.; Hou, Y.-J.; Pan, M.; Zhang, L.-Y.; Chen, L.; Su, C.-Y. Homochiral D4-symmetric metal – organic cages from stereogenic Ru(II) metalloligands for effective enantioseparation of atropisomeric molecules, *Nature Commun.* **2016**, *7*, 10487.

(16) (a) Dong, J.; Zhou, Y.; Zhang, F.; Cui, Y. A Highly Fluorescent Metallosalalen-Based Chiral Cage for Enantioselective Recognition and Sensing, *Chem. -Eur. J.* **2014**, *20*, 6455–6461. (b) Pan, M.; Wu, K.; Zhang, J.-H.; Su, C.-Y. Chiral Metal–Organic Cages/Containers (MOCs): From Structural and Stereochemical Design to Applications, *Coord. Chem. Rev.* **2019**, 37⁸, 333–349.

(17) (a) Tan, C.; Jiao, J.; Li, Z; Liu, Y.; Han, X.; Cui, Y. Design and Assembly of a Chiral Metallosalen-Based Octahedral Coordination Cage for Supramolecular Asymmetric Catalysis, *Angew. Chem. Int. Ed.* **2018**, *57*, 1–7. (b) Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. Supramolecular Catalysis in Metal-Ligand Cluster Hosts, *Chem. Rev.* **2015**, *115*, 3012–3035. (c) Zhao, C.; Sun, Q.-F.; Hart-Cooper, W. M.; DiPasquale, A. G.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. Chiral Amide Directed Assembly of a Diastereo- and Enantiopure Supramolecular Host and its Application to Enantioselective Catalysis of Neutral Substrates, *J. Am. Chem. Soc.* **2013**, *135*, 18802–18805.

(18) Chen, L.-J.; Yang, H.-B.; Shionoya, M. Chiral metallosupramolecular architectures, *Chem. Soc. Rev.* 2017, *46*, 2555–2576.

(19) (a) Rizzuto, F. J.; Pröhm, P.; Plajer, A. J.; Greenfield, J. L.; Nitschke, J. R. Hydrogen-Bond-Assisted Symmetry Breaking in a Network of Chiral Metal-Organic Assemblies, *J. Am. Chem. Soc.* **2019**, *141*, 1707–1715. (b) Zhao, C.; Toste, F. D.; Raymond, K. N.; Bergman, R. G. Nucleophilic Substitution Catalyzed by a Supramolecular Cavity Proceeds with Retention of Absolute Stereochemistry, *J. Am. Chem. Soc.* **2014**, *136*, 14409–14412. (c) Argent, S. P.; Riis-Johannessen, T.; Jeffery, J. C.; Harding, L. P.; Ward, M. D. Diastereoselective Formation and Optical Activity of an M_4L_6 Cage Complex, *Chem. Commun.* **2005**, *4647–4649*.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

60

(20) (a) Davis, A. V.; Fiedler, D.; Ziegler, M.; Terpin, A.; Raymond, K. N. Resolution of Chiral, Tetrahedral M_4L_6 Metal-Ligand Hosts, *J. Am. Chem. Soc.* 2007, *129*, 15354–15363.

(21) (a) Wan, S.; Lin, L.-R.; Zeng, L.; Lin, Y.; Zhang, H. Efficient Optical Resolution of Water-Soluble Self-Assembled Tetrahedral M₄L₆ Cages with 1,1'-Bi-2-Naphthol, *Chem. Commun.* **2014**, *50*, 15301–15304.

(22) (a) Bing, T. Y.; Kawai, T.; Yuasa, J. Ligand-to-Ligand Interactions That Direct Formation of D₂-Symmetrical Alternating Circular Helicate, *J. Am. Chem. Soc.* 2018, 140, 3683– 3689. (b) Nishioka, Y.; Yamaguchi, T.; Kawano, M.; Fujita, M. Asymmetric [2 + 2] Olefin Cross Photoaddition in a Self-Assembled Host with Remote Chiral Auxiliaries, *J. Am. Chem. Soc.* 2008, 130, 8160–8161.

(23) (a) Yan, L.-L.; Tan, C.-H.; Zhang, G.-L.; Zhou, L.-P.; Bünzli, J.-C.; Sun, Q.-F. Stereocontrolled Self-Assembly and Self-Sorting of Luminescent Europium Tetrahedral Cages, *J. Am. Chem. Soc.* **2015**, *137*, 8550–8555.

(24) Li, X.-Z.; Zhou, L.-P.; Yan, L.-L.; Yuan, D.-Q.; Lin, C.-S.; Sun, Q.-F. Evolution of Luminescent Supramolecular Lanthanide M_{2n}L_{3n} Complexes from Helicates and Tetrahedra to Cubes, *J. Am. Chem. Soc.* **2017**, *139*, **8237**–8244.

(25) Wu, Z.; Zhou, K.; Ivanov, A. V.; Yusobov, M.; Verpoort, F. The Simplest and Fascinating Metal-Organic Polyhedra: Tetrahedra, *Coord. Chem. Rev.* **2017**, 353, 180–200.

(26) (a) Furusho, Y.; Kimura, T.; Mizuno, Y.; Aida, T. Chirality-Memory Molecule: A *D*₂-Symmetric Fully Substituted Porphyrin as a Conceptually New Chirality Sensor, *J. Am. Chem. Soc.* **1997**, *119*, 5267–5268. (b) Yashima, E.; Maeda, K.; Okamoto, Y. Memory of macromolecular helicity assisted by interaction with achiral small molecules, *Nature* **1999**, 399, 449–451.

(27) (a) McTernan, C. T.; Ronson, T. K.; Nitschke, J. R. Postassembly Modification of Phosphine Cages Controls Host–Guest Behavior, *J. Am. Chem. Soc.* **2019**, *141*, 6837–6842.

(28) Liu, T.; Liu, Y.; Xuan, W.; Cui, Y. Chiral Nanoscale Metal-Organic Tetrahedral Cages: Diastereoselective Self-Assembly and Enantioselective Separation, *Angew. Chem. Int. Ed.* **2010**, *49*, 4121– 4124.

(29) Telfer, S. G.; McLean, T. M.; Waterland, M. R. Exciton Coupling in Coordination Compounds, *Dalton Trans.* 2011, 40, 3097–3108.

(30) (a) Muller, G. Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials (Ed.: A. de Bettencourt-Dias), Wiley, Hoboken **2014**, pp. 77–124.

(31) (a) Bonsall, S. D.; Houcheime, M.; Straus, D. A.; Muller, G. Optical Isomers of N,N'-Bis(1-phenylethyl)-2,6pyridinedicarboxamide Coordinated to Europium(III) Ions as Reliable Circularly Polarized Luminescence Calibration Standards. *Chem. Commun.* **2007**, *35*, 3676–3678. (b) Petoud, S.; Muller, G.; Moore, E. G.; Xu, J.; Sokolnicki, J.; Riehl, J. P.; Le, U. N.; Cohen, S. M.; Raymond, K. N. Brilliant Sm, Eu, Tb, and Dy Chiral Lanthanide Complexes with Strong Circularly Polarized Luminescence. *J. Am. Chem. Soc.* **2007**, *129*, 77–83.

(32) Hua, K. T.; Xu, J.; Quiroz, E. E.; Lopez, S.; Ingram, A. J.; Johnson, V. A.; Tisch, A. R.; de Bettencourt-Dias, A.; Straus, D. A.; Muller, G. Structural and Photophysical Properties of Visible- and Near-IR-Emitting Tris Lanthanide(III) Complexes Formed with the Enantiomers of N,N'-Bis(1-phenylethyl)-2,6pyridinedicarboxamide, *Inorg. Chem.* **2012**, *51*, 647–660.

(33) (a) Clegg, J. K.; Cremers, J.; Hogben, A. J.; Breiner, B.; Smulders, M. M. J.; Thoburnad, J. D.; Nitschke, J. R. A Stimuli Responsive System of Self-Assembled Anion-Binding $Fe_4L_6^{8+}$ cages, *Chem. Sci.* **2013**, *4*, 68–76.

(34) Dutra, J. D. L.; Bispo, T. D.; Freire, R. O. LUMPAC Lanthanide Luminescence Software: Efficient and User Friendly, *J. Comput. Chem.* **2014**, *35*, 772–775.

(35) (a) Castilla, A. M.; Ousaka, N.; Bilbeisi, R. A.; Valeri, E.; Ronson, T. K.; Nitschke, J. R. High-Fidelity Stereochemical Memory in a $\text{Fe}^{II}_{4}L_{4}$ Tetrahedral Capsule, *J. Am. Chem. Soc.* **2013**, *135*, *17999–18066*. (b) Ziegler, M.; Davis, A. V.; Johnson, D. W.; Raymond, K. N. Supramolecular Chirality: A Reporter of Structural Memory, *Angew. Chem. Int. Ed.* **2003**, *42*, 665–668.

(36) The measurement methods for obtaining the ee values of cage-2 include the employment of chiral NMR chemical shifts and chiral HPLC technologies. In view of the strong eletrophilicity of trifluoroacetyl of ligand, we selected kinds of chiral agents, such as those of chiral amine, chiral alcohol, chiral carboxylic ether, and chiral amino acid etc., as chemical shift agent to determine the ¹H, ³P, ¹⁹F NMR of the cages. In HPLC, chiral chromatographic columns of "CHIRALPAK IA, IB, IC, ID" are employed.

(37) (a) Miyata, K.; Nakagawa, T.; Kawakami, R.; Kita, Y.; Sugimoto, K.; Nakashima, T.; Harada, T.; Kawai, T.; Hasegawa, Y. Remarkable Luminescence Properties of Lanthanide Complexes with Asymmetric Dodecahedron Structures, *Chem. -Eur. J.* 2011, *17*, 521–528.





