

**Supporting Information for**  
**Structural Relaxation Chirality Transfer Enhanced Circularly**  
**Polarized Luminescence in Heteronuclear Ce<sup>III</sup>-Mn<sup>II</sup> Complexes**

*Huanyu Liu, Gang Yu, Peihao Huo, Ruoyao Guo, Yujia Li, Hao Qi, Jiayin Zheng, Tong Jin, Zifeng Zhao,  
Zuqiang Bian, Zhiwei Liu\**

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials  
Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University,  
Beijing 100871, China

Email: zwliu@pku.edu.cn

**Contents**

<b>1. Experimental Details.....</b>	<b>2</b>
<b>1.1 Chemicals and Synthesis.....</b>	<b>2</b>
<b>1.2 Characterization Methods.....</b>	<b>2</b>
<b>2. Structure and Photophysics .....</b>	<b>4</b>
<b>3. Reference.....</b>	<b>10</b>

# 1. Experimental Details

## 1.1 Chemicals and Synthesis

The metal halides CeBr<sub>3</sub> (99.99%, Grimm Advanced Materials), MnBr<sub>2</sub> (99%, Macklin), LaBr<sub>3</sub> (99.9%, Aladdin), and ZnBr<sub>2</sub> (98%, D&B) were commercially available and were used as received. All other chemical reagents were of reagent-grade purity or better and were used directly as commercially available states without other purification unless otherwise mentioned. The synthesis and pretreatment for characterization of complexes were conducted in a dry glovebox filled with nitrogen. Dichloromethane (DCM) was distilled using CaH<sub>2</sub> under a nitrogen atmosphere. Extra dry solvents such as methanol (MeOH) and n-butanol (BuOH) were degassed before used in the glovebox.

Ligands (**R/S**)-**L** [(2*R*, 3*R*)- or (2*S*, 3*S*)-2,3-dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane] were synthesized following published procedures <sup>1</sup>.

**Synthesis of (R)-CeMn:** (**R**)-**L** (196.8 mg, 0.6731 mmol, dissolved in 2 mL extra dry MeOH) was added into CeBr<sub>3</sub> (234.2 mg, 0.6166 mmol, dissolved in 5 mL extra dry MeOH) under magnetic stirring and then MnBr<sub>2</sub> (127.8 mg, 0.5950 mmol, dissolved in 3 mL extra dry MeOH) was added into the mixture. Subsequently, 1 mL extra dry BuOH was added. After slow evaporation, the resulting pale-yellow block crystals were filtered and washed by BuOH to yield (**R**)-**CeMn** as a pale-yellow solid (222.2 mg, 41%). Some of these crystals were qualified for single crystal X-ray diffraction. Elemental analysis calcd (%) for C<sub>28</sub>H<sub>58.58</sub>Br<sub>5.42</sub>Ce<sub>2</sub>MnO<sub>14.58</sub>·BuOH: C 26.04, H 4.70; found: C 26.19, H 4.50.

**Synthesis of (S)-CeMn:** (**S**)-**CeMn** was synthesized through similar procedures of (**R**)-**CeMn**, but instead (**S**)-**L** (195.6 mg, 0.6689 mmol), CeBr<sub>3</sub> (234.6 mg, 0.6177 mmol) and MnBr<sub>2</sub> (134.3 mg, 0.6220 mmol) were used. (**S**)-**CeMn** was obtained as a pale-yellow solid (338.2 mg, 63%). Elemental analysis calcd (%) for C<sub>28</sub>H<sub>58.52</sub>Br<sub>5.48</sub>Ce<sub>2</sub>MnO<sub>14.52</sub>·BuOH: C 26.06, H 4.68; found: C 26.00, H 4.68.

**Synthesis of (S)-CeZn:** (**S**)-**CeZn** was synthesized through similar procedures of (**R**)-**CeMn**, but instead (**S**)-**L** (340 mg, 1.16 mmol), CeBr<sub>3</sub> (352.6 mg, 0.9284 mmol) and ZnBr<sub>2</sub> (211.6 mg, 0.9396 mmol) were used. (**S**)-**CeZn** was obtained as a white solid (35.1 mg, 3.9%). Elemental analysis calcd (%) for C<sub>16</sub>H<sub>36</sub>Br<sub>5</sub>CeO<sub>8</sub>Zn: C 19.99, H 3.77; found: C 19.76, H 3.64.

**Synthesis of (S)-LaMn:** (**S**)-**LaMn** was synthesized through similar procedures of (**R**)-**CeMn**, but instead (**S**)-**L** (99.2 mg, 0.3393 mmol), LaBr<sub>3</sub> (119.7 mg, 0.3162 mmol) and MnBr<sub>2</sub> (68.3 mg, 0.318 mmol) were used. (**S**)-**LaMn** was obtained as a pale-yellow solid (205.4 mg, 75%). Elemental analysis calcd (%) for C<sub>28</sub>H<sub>58.39</sub>Br<sub>5.61</sub>La<sub>2</sub>MnO<sub>12</sub>·1.3BuOH: C 26.54, H 4.79; found: C 26.54, H 4.80.

## 1.2 Characterization Methods

### Elemental analysis

Elemental analyses were performed on a VARIO EL analyzer (GmbH, Hanau, Germany).

### **Single crystal structure measurements**

The single crystal X-ray diffraction (SCXRD) data were collected on a Rigaku Mercury CCD diffractometer. The radiation used in the SCXRD analysis is the graphite-monochromated Mo K $\alpha$  emission line ( $\lambda = 0.71069 \text{ \AA}$ ). SCXRD data were collected by using the CrystalClear software. Structural refinements were conducted with SHELXL-97 or SHELXL-2013 software.

### **Sample preparation method for photophysical properties test**

All solid powder samples were encapsulated between two quartz plates (20 $\times$ 20 $\times$ 1 mm) by paraffin. The commercially available paraffin was further purified by oxidation using KMnO $_4$  and activated carbon to remove fluorescent whitening agents.

### **Steady state and transient state PL**

Steady state and transient state PL spectra were measured on an Edinburgh Analytical Instruments FLS980 spectrophotometer with Xe lamp, microsecond pulse lamp and pulsed lasers (Edinburgh). The transient state PL spectra data (emission decay curves) were analyzed by tail fit of the decay profile using a software package provided by Edinburgh Instruments to obtain the lifetime data. The quality of the fits was evidenced by appropriate  $\chi^2$  values ( $0.8 < \chi^2 < 1.3$ ). All measurements were performed under room temperature.

### **PLQY test**

PLQYs were measured in Hamamatsu C9920-02 absolute quantum yield measurement system with an integrating sphere. The relative error of PLQY test is around  $\pm 5\%$ .

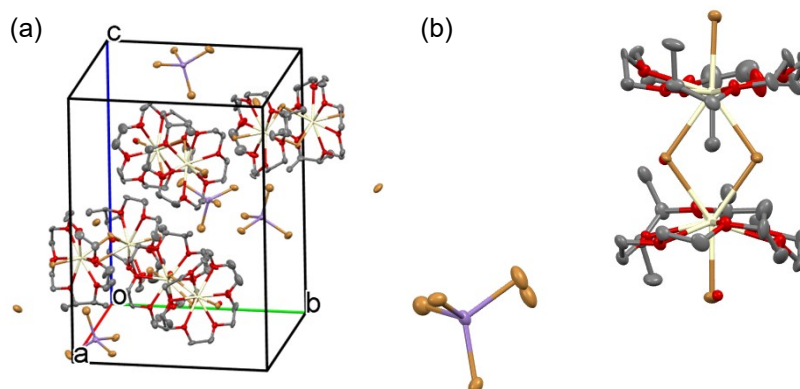
### **CPL test**

The CPL spectra for polycrystalline samples were recorded on a JASCO CPL-300 spectrometer. The polycrystalline samples ( $\sim 10 \text{ mg}$ ) were mixed with polymethylmethacrylate (250 mg in 1 mL DCM) to yield uniform suspensions, which were sealed in capped cuvettes under N $_2$  atmosphere before tests. Suspensions rather than compacted powders between quartz plates were used to reduce the influence of reflection. The scanning speed was  $100 \text{ nm} \cdot \text{min}^{-1}$ . Numbers of accumulations in each measurement were higher than 6. The excitation slit-width and the emission slit-width were  $3000 \text{ \mu m}$ .

## 2. Structure and Photophysics

**Table S1.** Crystallographic data of (*R*)-CeMn. Further details of the crystal structure investigation can be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2380143.

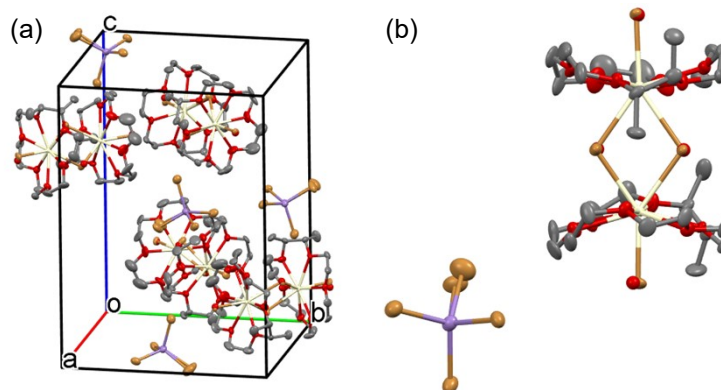
Compound	( <i>R</i> )-CeMn
Formula	C <sub>28</sub> H <sub>58.58</sub> Br <sub>5.42</sub> Ce <sub>2</sub> MnO <sub>14.58</sub>
Mw	1396.90
Crystal system	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	15.2440(3)
<i>b</i> (Å)	15.3069(3)
<i>c</i> (Å)	21.3108(4)
<i>α</i> (°)	90
<i>β</i> (°)	90
<i>γ</i> (°)	90
<i>V</i> (Å <sup>3</sup> )	4972.63(17)
<i>Z</i>	4
<i>T</i> (K)	120.01(15)
<i>θ</i> range (°)	1.638 – 30.751
<i>d</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	1.866
F (000)	2696
Crystal size (mm)	0.2 × 0.15 × 0.03
Absorp. coeff. (mm <sup>-1</sup> )	6.456
Index range	-12 ≤ <i>h</i> ≤ 19 -19 ≤ <i>k</i> ≤ 11 -27 ≤ <i>l</i> ≤ 24
Reflns collected	23179 (R <sub>int</sub> = 0.0279)
Indep. reflns	12217
Reflns obs. [ <i>I</i> > 2σ( <i>I</i> )]	10142
data/restr/paras	12217/73/504
GOF	1.066
R <sub>1</sub> /wR <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0446/0.1122
R <sub>1</sub> /wR <sub>2</sub> (all data)	0.0591/0.1186
Largest diff. peak & hole (e/Å <sup>3</sup> )	1.535/-2.266



**Figure S1.** Single-crystal structures showing as ellipsoids at the 50% probability level for (*R*)-CeMn. All the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Ce yellow, Mn purple, O red. (a) Unit cell; (b) Molecular structure.

**Table S2.** Crystallographic data of (**S**)-CeMn. Further details of the crystal structure investigation can be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2380144.

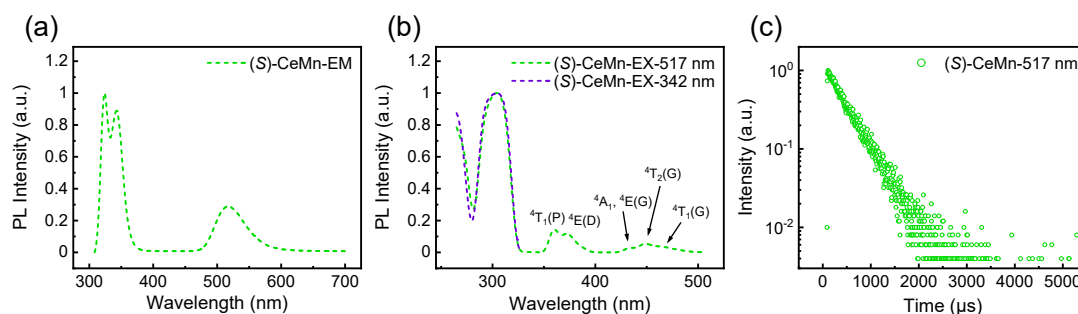
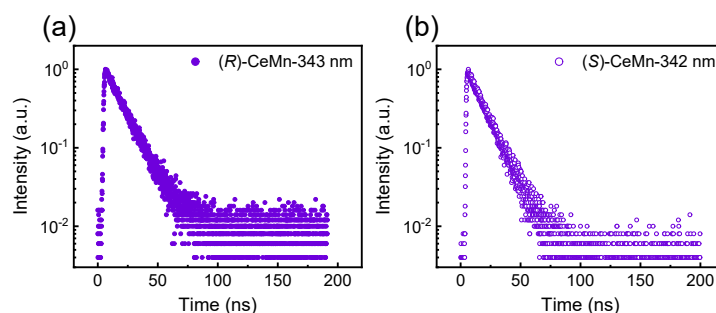
Compound	( <b>S</b> )-CeMn
Formula	C <sub>28</sub> H <sub>58.52</sub> Br <sub>5.48</sub> Ce <sub>2</sub> MnO <sub>14.52</sub>
Mw	1400.36
Crystal system	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	15.3088(3)
<i>b</i> (Å)	15.3451(3)
<i>c</i> (Å)	21.3976(4)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	5026.62(19)
<i>Z</i>	4
<i>T</i> (K)	180.00(10)
$\theta$ range (°)	1.879 – 30.836
<i>d</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	1.850
<i>F</i> (000)	2701
Crystal size (mm)	0.25 × 0.25 × 0.15
Absorp. coeff. (mm <sup>-1</sup> )	6.430
Index range	-19 ≤ <i>h</i> ≤ 20 -22 ≤ <i>k</i> ≤ 12 -27 ≤ <i>l</i> ≤ 27
Reflns collected	36019 ( <i>R</i> <sub>int</sub> = 0.0479)
Indep. reflns	13383
Refns obs. [ <i>I</i> > 2σ( <i>I</i> )]	10994
data/restr/paras	13383/90/497
GOF	1.046
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0616/0.1638
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0760/0.1700
Largest diff. peak & hole (e/Å <sup>3</sup> )	1.506/-1.805



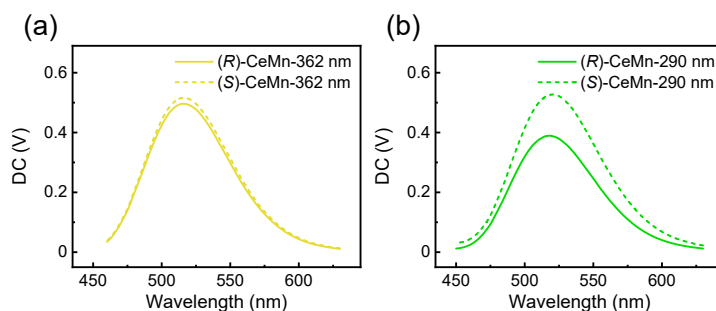
**Figure S2.** Single-crystal structures showing as ellipsoids at the 50% probability level for (**S**)-CeMn. All the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Ce yellow, Mn purple, O red. (a) Unit cell; (b) Molecular structure.

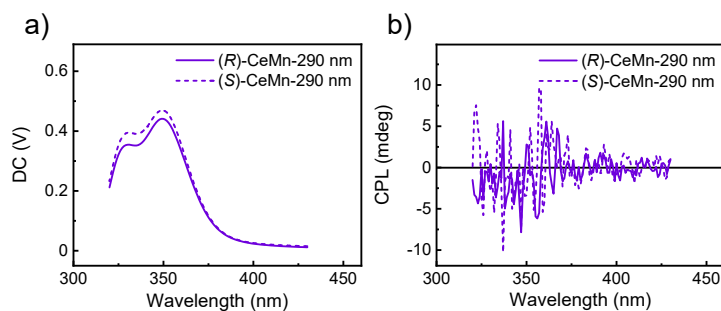
**Table S3.** Mn-Br bond lengths in (*R/S*)-CeMn.

Compound	( <i>R</i> )-CeMn	( <i>S</i> )-CeMn
	2.452	2.468
Mn-Br bond length (Å)	2.504	2.508
	2.510	2.508
	2.510	2.513

**Figure S3.** (a) Emission spectrum and (b) excitation spectra of (*S*)-CeMn in solid powder state; (c) transient decay spectrum of Mn(II)-center emission in solid (*S*)-CeMn. The detecting wavelengths were marked in the legend.**Figure S4.** Transient decay spectra of Ce<sup>III</sup>-center emission in solid (a) (*R*)-CeMn and (b) (*S*)-CeMn. The detecting wavelengths were marked in the legend.

**Note:** The PLQY tests of (*R/S*)-CeMn are affected by the sample states such as the size of grains and the amount of adsorbed solvent molecules. We tried our best to keep the preparation procedures of (*R/S*)-CeMn samples the same, but there still existed some differences due to the separately-conducted crystallization. The current data provided a preliminary description on the luminescence efficiency of (*R/S*)-CeMn.

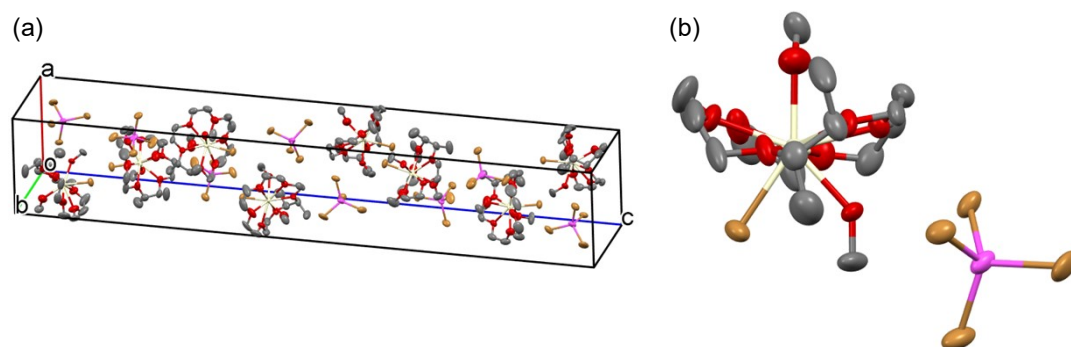
**Figure S5.** DC spectra of (*R/S*)-CeMn excited at (a) 362 nm and (b) 290 nm in solid powder state.



**Figure S6.** (a) DC spectra and (b) CPL spectra of the Ce<sup>III</sup>-center emission in solid (*R/S*)-CeMn. The excitation wavelength was 290 nm.

**Table S4.** Crystallographic data of (*S*)-CeZn. Further details of the crystal structure investigation can be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2380147.

Compound	( <i>S</i> )-CeZn
Formula	C <sub>16</sub> H <sub>36</sub> Br <sub>5</sub> CeO <sub>8</sub> Zn
Mw	961.49
Crystal system	Tetragonal
Space group	<i>P</i> 4 <sub>1</sub> 2 <sub>1</sub> 2
<i>a</i> (Å)	10.21080(16)
<i>b</i> (Å)	10.21080(16)
<i>c</i> (Å)	58.9846(14)
<i>α</i> (°)	90
<i>β</i> (°)	90
<i>γ</i> (°)	90
<i>V</i> (Å <sup>3</sup> )	6149.8(2)
<i>Z</i>	8
<i>T</i> (K)	179.99(10)
<i>θ</i> range (°)	2.024 - 28.039
<i>d</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	2.077
<i>F</i> (000)	3672
Crystal size (mm)	0.15 × 0.12 × 0.11
Absorp. coeff. (mm <sup>-1</sup> )	8.771
Index range	-8 ≤ <i>h</i> ≤ 11 -12 ≤ <i>k</i> ≤ 13 -77 ≤ <i>l</i> ≤ 65
Reflns collected	17728 ( <i>R</i> <sub>int</sub> = 0.0292)
Indep. reflns	7092
Refns obs. [ <i>I</i> > 2σ( <i>I</i> )]	5902
data/restr/paras	7092/28/290
GOF	1.023
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0431/0.0933
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0557/0.0978
Largest diff. peak & hole (e/Å <sup>3</sup> )	1.685/-0.795

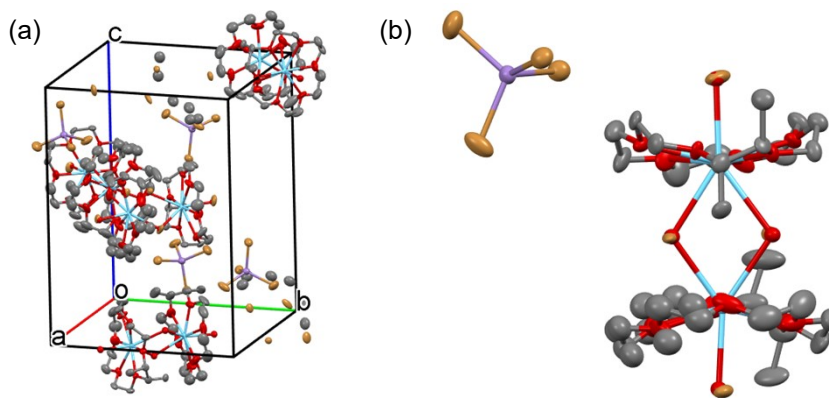


**Figure S7.** Single-crystal structures showing as ellipsoids at the 50% probability level for **(S)-CeZn**. All the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Ce yellow, Zn pink, O red. (a) Unit cell; (b) Molecular structure.

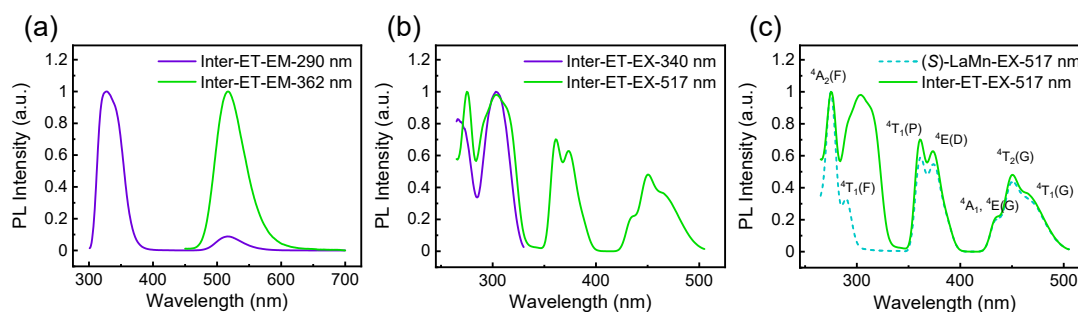
**Table S5.** Crystallographic data of **(S)-LaMn**. Further details of the crystal structure investigation can be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2380146.

Compound	<b>(S)-LaMn</b>
Formula	$C_{28}H_{58.39}Br_{5.61}La_2MnO_{14.39}$
Mw	1406.27
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
$a$ (Å)	15.5414(4)
$b$ (Å)	15.5635(4)
$c$ (Å)	21.4150(6)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	5179.8(2)
$Z$	4
$T$ (K)	180.01(11)
$\theta$ range (°)	1.617 – 25.026
$d_{\text{calc}}$ (g·cm <sup>-3</sup> )	1.803
$F(000)$	2707
Crystal size (mm)	0.2 × 0.04 × 0.04
Absorp. coeff. (mm <sup>-1</sup> )	6.234
Index range	-18 ≤ $h$ ≤ 18 -16 ≤ $k$ ≤ 18 -17 ≤ $l$ ≤ 25
Reflns collected	20157 ( $R_{\text{int}} = 0.0334$ )
Indep. reflns	8868
Refns obs. [ $I > 2\sigma(I)$ ]	7477
data/restr/paras	8868/257/483
GOF	1.047
$R_1/wR_2$ [ $I > 2\sigma(I)$ ]	0.0514/0.1328
$R_1/wR_2$ (all data)	0.0640/0.1391
Largest diff. peak & hole (e/Å <sup>3</sup> )	1.462/-1.019

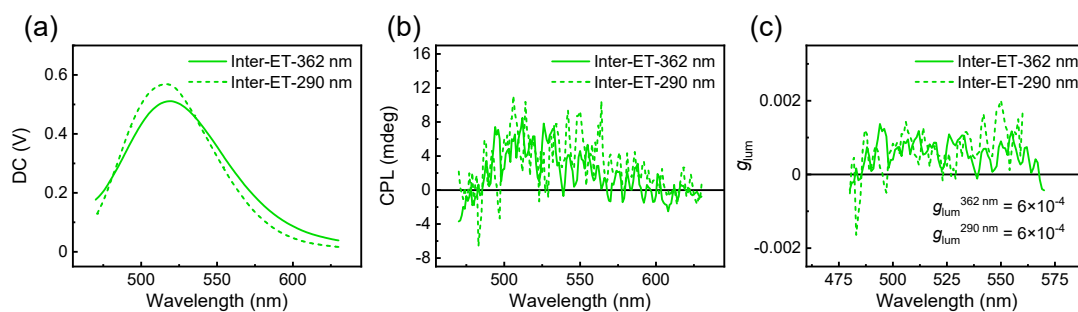




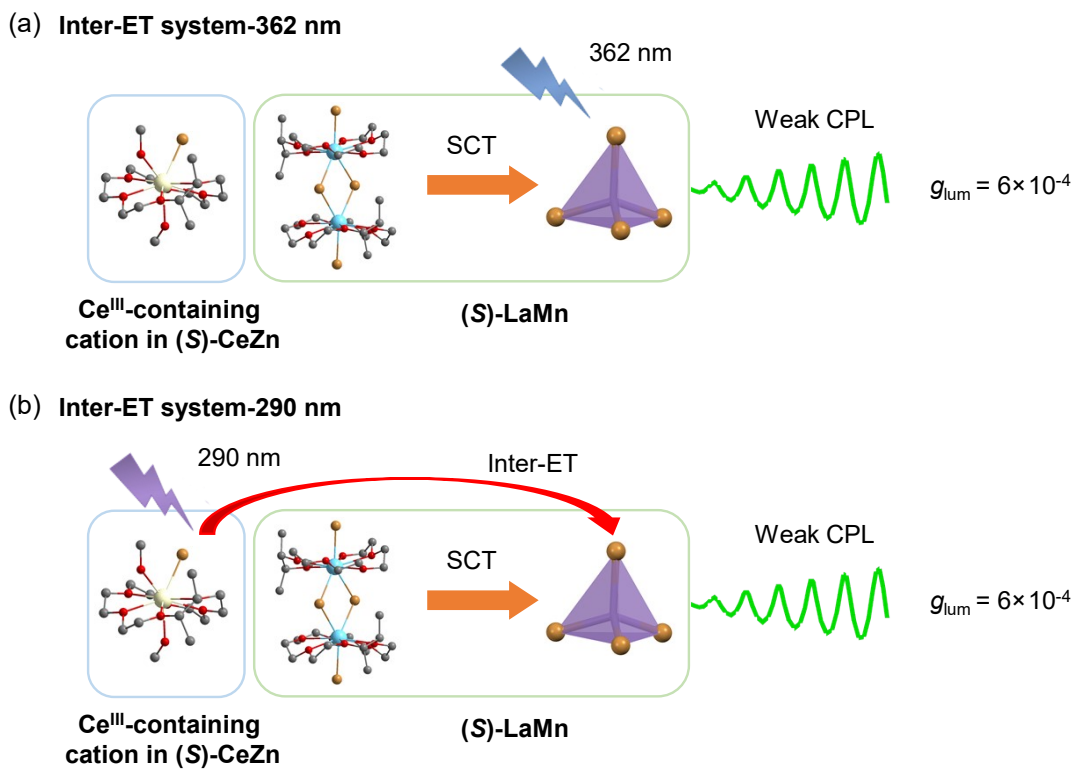
**Figure S8.** Single-crystal structures showing as ellipsoids at the 50% probability level for **(S)-LaMn**. All the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, La celeste, Mn purple, O red. (a) Unit cell; (b) Molecular structure.



**Figure S9.** (a) Emission spectrum and (b) excitation spectra of the Inter-ET system in solid powder state. (c) Excitation spectra of **(S)-LaMn** in solid powder state. The excitation wavelengths and the detecting wavelengths were marked in the legend. The Inter-ET system was prepared by mixing the solid powder of **(S)-CeZn** and **(S)-LaMn** directly to ensure the intermolecular energy transfer and no metathesis reaction happened.



**Figure S10.** (a) DC spectra, (b) CPL spectra and (c) the  $g_{lum}$  factors of the Inter-ET system in solid powder state. The excitation wavelengths were marked in the legend.



**Figure S11.** Schematic diagram of the chirality and energy transfer processes in the Inter-ET system. (a) While excited by 362 nm, the Mn<sup>II</sup>-center emission shows weak CPL caused by static chirality transfer (SCT); (b) While excited by 290 nm, the Mn<sup>II</sup>-center emission still shows weak CPL caused by SCT, though there exists intermolecular energy transfer (Inter-ET) from **(S)-CeZn**. Atom notation: C grey balls, Br brown balls, Ce yellow balls, La celeste balls, Mn purple polyhedrons, O red balls.

### 3. Reference

1. Naemura, K.; Ueno, M., Synthesis and enantiomer recognition of the 18-crown-6 derivative containing two tert-butyl substituents as a chiral barrier. *Bull. Chem. Soc. Jpn.*, **1990**, *63*, 3695-3697.