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ARTICLE TYPE

A pair of dinuclear Re(I) enantiomers: synthesis, crystal structures, chiroptical and ferroelectric properties†

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The reaction of enantiomeric bis-bidentate bridging ligands (+)/(–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S/L_R) with $[\text{Re}(\text{CO})_5\text{Cl}]$ yielded a pair of dinuclear Re(I) enantiomers formulated as $[\text{Re}_2(L_S/L_R)(\text{CO})_6\text{Cl}_2] \cdot 4\text{CH}_2\text{Cl}_2$ (**R-1** and **S-1**, the isomers containing the respective L_R and L_S ligands). They were characterized by elemental analyses, IR spectra and X-ray crystallography. Circular dichroism spectra verified their chiroptical activities and enantiomeric natures. The measurements of second harmonic generation (SHG) and ferroelectric properties showed that **R-1** displays nonlinear optical (NLO) activity and ferroelectricity with the remnant polarization (P_r) of $1.6 \mu\text{C}/\text{cm}^2$ under an applied field of $7.3 \text{ kV}/\text{cm}$ at room temperature. **R-1** and **S-1** represent the first example of polynuclear Re(I) complexes with ferroelectric property. Notably, the P_r value is much larger than that of reported mononuclear chiral Re(I) analogue. In particular, unlike mononuclear Re(I) complexes with the type of $[\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{N})(\text{X})]$ ($\text{N}^{\wedge}\text{N}$ = diimine and X = halides), which usually exhibit intense emission in the visible range, **R-1** and **S-1** do not show any detectable emission at any temperature range and the reason of nonluminescence for **R-1** and **S-1** was further elucidated in this work. Moreover, our research results also elucidated that the Re nuclearity has a great influence on not only emitting property but also ferroelectric behavior.

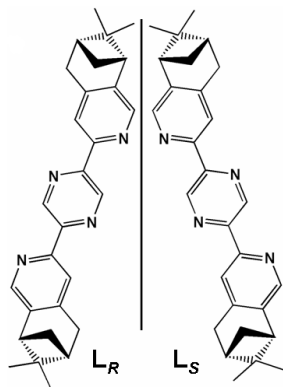
Introduction

Recently, there has been growing interest in the design and synthesis of homochiral complexes in view of their promising applications in enantioselective separation and catalysis, nonlinear optics and chiral sensors.¹ In particular, chiral complexes may possess peculiar physical properties such as magneto-chiral dichroism (MChD), second-order nonlinear optical (NLO) and ferroelectricity, which are only based on the chiral molecular structures or noncentrosymmetric molecular arrangements.² Therefore, all these characters can endue chiral complexes with a multifunctional feature. Usually, two distinct strategies were exploited to prepare chiral complexes: (1) utilizing chiral bridging ligands to connect the adjacent metal centres or secondary building units, then straightforwardly transferring chiral information into the resultant complexes,³ and (2) use of achiral starting materials without any chiral sources via spontaneous resolution, resulting in the formation of chiral molecular structures.⁴ It is desired to obtain the chiral complexes via the second strategy. However, this approach usually affords a racemic mixture without any chiroptical property.⁵ So, the usage of enantiopure chiral ligands has proven to be the most reliable approach to transfer and control the chiral information in the molecular self-assembly systems.^{2e-i}

On the other hand, Re(I) tricarbonyl diimine complexes with the type of *fac*- $[\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{N})(\text{X})]$ (where $\text{N}^{\wedge}\text{N}$ = diimine and X = halides) are becoming increasingly attractive owing to their

tunable photophysical properties and potential applications including solar energy conversion, light emitting devices, photovoltaics and photocatalysis.⁶ In this context, mononuclear Re(I) complexes are the most prevalent in the literature,⁶ and only a limited number of dinuclear and multinuclear Re(I) assemblies with crystallographic evidence were reported.⁷ Among them, the chiral Re(I) complexes remain rarely explored mainly due to the fact that the available chiral diimine ligands are very scarce.^{6f,8} Recently, we reported a chiral mononuclear Re(I) tricarbonyl diimine complex $\text{Re}(\text{CO})_3(L_{RR})\text{Cl}$ (L_{RR} = (–)-4,5-pinene-2,2'-bipyridine) obtained via the reaction of chiral diimine ligand L_{RR} with $\text{Re}(\text{CO})_5\text{Cl}$.^{6f} Meanwhile, its photophysical and ferroelectric properties were also investigated in detail. As the extension of our research work, we expect to prepare enantiopure dinuclear Re(I) complexes and then explore their corresponding physical properties. To realize this target, the design of a chiral bridging ligand is crucial. An effective ligand should be homochiral and possesses at least two sets of coordinating sites, which must be separated by a rigid spacer so that each set of coordinating sites is able to accommodate targeted metal ions. Bearing this in mind, in this contribution, we designed such a bis-bidentate enantiomeric pair, (+)/(–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S/L_R , Scheme 1) as bis-chelating ligands to react with $\text{Re}(\text{CO})_5\text{Cl}$, respectively. Subsequently, a pair of dinuclear Re(I) enantiomer with the formula of $[\text{Re}_2(L_R/L_S)(\text{CO})_6\text{Cl}_2] \cdot 4\text{CH}_2\text{Cl}_2$ (**R-1** and **S-1**, the isomers containing the respective L_R and L_S ligands) were stereoselectively synthesized. Notably, **R-1** showed nonlinear

optical activity and room-temperature ferroelectric property with the remnant polarization (P_r) of $1.6 \mu\text{C}/\text{cm}^2$ under an applied field of $7.3 \text{ kv}/\text{cm}$, representing the first example of homochiral polynuclear Re(I) complex with ferroelectric property. In contrast to reported chiral mononuclear Re(I) analogue,^{6f} **R-1** does not display any emission. Herein, we reported the synthesis, crystal structures and physical properties of **R-1** and **S-1**.



Scheme 1 Enantiomeric bis-bidentate bridging ligands L_R and L_S .

10 Experimental

Materials and general methods

All of the chemicals are commercially available and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were registered on a TENSOR27 Bruker Spectrophotometer from KBr pellets in the region of $4000\text{--}400 \text{ cm}^{-1}$. UV-vis absorption spectra were obtained on a UV-4802 Spectrometer. The solid-state CD spectra were performed on a JASCO J-810 Spectropolarimeter from KCl pellets (1% Wt.) at room temperature. The P - E hysteresis loops of **R-1** and **S-1** were obtained with Precision Multiferroic Ferroelectric Tester made by Radiant Technologies Inc. at room temperature. For example, single crystal of **R-1** with an approximate size of $1.3 \times 0.9 \times 0.7 \text{ mm}^3$ was carefully connected to the instrument with electrodes made of Cu wire of $120 \mu\text{m}$ diameter covered by Ag-conducting glue on two opposite surfaces of a crystal. The SHG properties of **R-1** and **S-1** were tested by the method of Kurtz and Perry using an Nd:YAG laser (1064 nm) with input pulse of 350 mV.⁹ KDP powders were measured as a reference to assess the SHG efficiencies of **R-1** and **S-1**.

Synthesis of $[\text{Re}_2(L_R)(\text{CO})_6\text{Cl}_2] \cdot 4\text{CH}_2\text{Cl}_2$ (**R-1**)

A total of 42 mg of $(-)$ -2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_R , 0.1 mmol) and 2 equiv. of $\text{Re}(\text{CO})_5\text{Cl}$ (72 mg, 0.2 mmol) were refluxed in 20 mL toluene for 12 hours under an N_2 atmosphere. A colour change from yellow to brown was observed. The reaction mixture was allowed to cool to room temperature and the solvent was removed under vacuum. The crude solid was dissolved in CH_2Cl_2 , then filtered, and **R-1** as dark-brown solid was obtained by adding Et_2O (Yield: 98 mg, 72%). Slow diffusion of diethyl ether into a CH_2Cl_2 solution of **R-1** led to the isolation of single crystals for X-ray diffraction analysis. Elemental analyses calcd (%) for **R-1** ($\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_6\text{Cl}_{10}\text{Re}_2$,

1373.62): C 33.22, H 2.79, N 4.08; found: C 33.39, H 2.65, N 4.13. IR (cm^{-1} , KBr disc): $\nu_{\text{C}=\text{O}} = 2019(\text{S})$, $\nu_{\text{C}=\text{O}} = 1907(\text{S})$, $\nu_{\text{C}=\text{C}} = 1611(\text{W})$.

Synthesis of $[\text{Re}_2(L_S)(\text{CO})_6\text{Cl}_2] \cdot 4\text{CH}_2\text{Cl}_2$ (**S-1**)

S-1 was obtained as dark-brown crystals by a method similar to that of **R-1**, except that $(+)$ -2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S) was used instead of $(-)$ -2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_R). Yield: 109 mg, 79%. Elemental analyses calcd (%) for **S-1** ($\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_6\text{Cl}_{10}\text{Re}_2$, 1373.62): C 33.22, H 2.79, N 4.08; found: C 33.36, H 2.88, N 4.17. IR (cm^{-1} , KBr disc): $\nu_{\text{C}=\text{O}} = 2021(\text{S})$, $\nu_{\text{C}=\text{O}} = 1905(\text{S})$, $\nu_{\text{C}=\text{O}} = 1609(\text{W})$.

X-ray crystallography

The crystal structures of **R-1** and **S-1** were determined on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Data reductions were made with the Bruker SAINT package. Absorption corrections were performed using the SADABS program. The structures were solved by direct methods and refined on F^2 by full matrix least-squares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model. All computations were carried out using the SHELXTL-2000 program package. Detailed crystallographic data and structures refinement parameters for enantiomeric pair **R-1** and **S-1** are summarized in Table 1. Selected bond distances and angles of **R-1** and **S-1** are listed in Table S1 (in ESI†).

Results and discussion

The bis-bidentate ligands L_R and L_S were synthesized according to similar procedures.¹⁰ The reaction of $\text{Re}(\text{CO})_5\text{Cl}$ with L_R or L_S (2:1 molar ratio) in toluene afforded the dark-brown solid of **R-1** or **S-1**. X-ray crystallographic analyses revealed that **R-1** and **S-1** are a pair of enantiomers and crystallize in the identical chiral space group $P2_1$ with the Flack values being 0.01(3) and 0.02(3) for **R-1** and **S-1**, respectively, suggesting that chirality deriving from chiral bridging ligand (L_R or L_S) has been transferred successfully into resulting solid structures. They show similar physical properties. Thus only the results of **R-1** are described in detail.

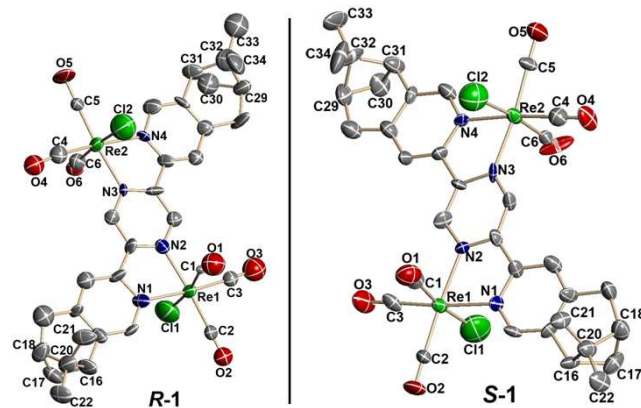


Fig. 1 ORTEP representation (50% probability ellipsoids) and enantiomeric pair of **R-1** and **S-1**; H atoms and solvent molecules were omitted for clarity.

Crystal structure of *R*-1

As shown in Fig. 1, *R*-1 is a dinuclear Re(I) complex and the asymmetric unit contains two Re(I) cations, six tricarbonyl moieties, a neutral bis-bidentate bridging ligand L_R , two Cl⁻ anions and four lattice CH₂Cl₂ molecules. The bridging ligand L_R links two Re(I) centers with the Re...Re separation of 7.084 Å and each Re(I) centre adopts a distorted octahedral coordination environment with N–Re–N bite angles of 74.9° and 74.5° for respective Re1 and Re2, which are smaller than the angle of 90° adopted in ideal octahedral geometry owing to the structural restriction of the chiral ligand L_R . The distances of Re–C and Re–N are in the range of 1.83(3)–1.93(2) and 2.145(18)–2.168(19) Å, respectively, which are commonly observed in other reported Re(I) tricarbonyl diimine complexes.^{7h,11} It is noteworthy that the bond lengths of Re–Cl are 2.402(13) and 2.420(12) in *R*-1, respectively, being obviously shorter than those of mononuclear Re(I) tricarbonyl complexes with weaker π -acceptor diimine ligands such as 2,2'-bipyridine ($d_{\text{Re-Cl}} = 2.476(2)$ Å),¹² 2,2':6',2''-terpyridine derivatives ($d_{\text{Re-Cl}} = 2.482(2)$ Å)¹³ and (-)-4,5-pinene-2,2'-bipyridine ($d_{\text{Re-Cl}} = 2.471(4)$ Å).^{6f} The similar results are also observed in dinuclear Re(I) tricarbonyl complex (μ -Me₂BPTZ)(Re(CO)₃Cl)₂ ($d_{\text{Re-Cl}} = 2.446(4)$ Å and Me₂BPTZ = 3,6-(5-methylpyridyl)-1,2,4,5-tetrazine, a linear bis-chelating ligand).⁷ⁱ It is suggested that the stronger π -accepting ability of the linear ligand L_R can lead to the generation of more electropositive character at Re(I) centre, thus facilitating electrostatically a stronger and shorter Re–Cl bond.⁷ⁱ

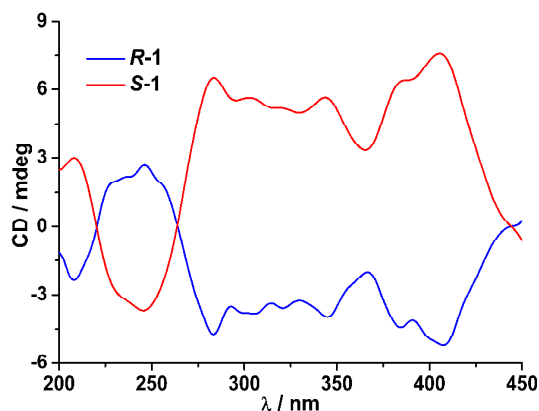


Fig. 2 The solid-state CD spectra of *R*-1 and *S*-1.

Circular dichroism (CD) spectra

To prove the chiroptical activities and enantiomeric natures of *R*-1 and *S*-1, their solid-state circular dichroism (CD) spectra were recorded based on a pressed KCl disk including 1% (w/w) of respective enantiopure crystal grains at room temperature. As shown in Fig. 2, *R*-1 and *S*-1 show typical exciton splitting patterns with positive and negative signals implying considerable chiroptical activities, and exhibit nice mirror-symmetrical CD spectra of one another in solid, which are indicative of their enantiomeric natures. The CD spectrum of *R*-1 displays negative Cotton effects at $\lambda_{\text{max}} = 283$ and 410 nm with positive one at $\lambda_{\text{max}} = 246$ nm, while *S*-1 shows Cotton effects with opposite signs at the same wavelengths. The results are accord with the structures obtained by single crystal X-ray diffraction. Furthermore, the

NLO-activities of *R*-1 and *S*-1 were ascertained by performing second harmonic generation (SHG) experiment using Kurtz and Perry method.¹⁴ We estimated the second-order NLO effect of *R*-1 and *S*-1, which show the SHG efficiencies approximately 1.5 and 1.2 times that of KDP (KH₂PO₄) for *R*-1 and *S*-1, respectively.

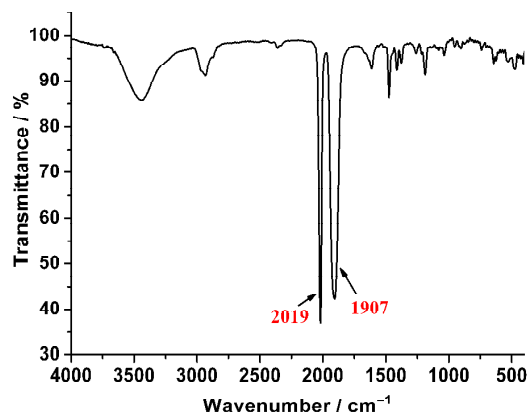


Fig. 3 FT-IR spectrum of *R*-1.

FT-IR spectroscopic study

The *face*-[Re(CO)₃(N[^]N)(X)]-type complexes in general display three intense IR absorptions in the 2020 and 1900 cm⁻¹ region. The sharp band at higher frequency (~2020 cm⁻¹) is attributed to the A'(1) mode (totally symmetric in-phase stretching vibration absorptions of the three C≡O ligands) and the remaining two bands at intermediate and lower frequencies are assigned to the A'(2) mode (totally symmetric out-phase stretching of the three C≡O ligands) and the A'' modes (asymmetric stretching of equatorial C≡O ligands).¹⁵ The reported dinuclear Re(I) complexes, such as [Re(CO)₃(Cl)]₂(dpq) (2025, 1922, 1902 cm⁻¹ and dpq = 2,3-bis(2-pyridyl)quinoxaline) and [Re(CO)₃(Cl)]₂(Me₂BPTZ) (2016, 1954 and 1929 cm⁻¹)^{7b,i} also exhibited three intense C≡O absorption bands. However, *R*-1 only shows two intense IR bands at 2019 and 1907 cm⁻¹ (Fig. 3). The similar FT-IR result was also obtained in *S*-1 complex (Fig. S1, ESI[†]). The reason is that the A'(2) and A'' bands are superimposed into a single broad band.¹⁶ To the best of our knowledge, this phenomena has never been observed in the dinuclear Re(I) tricarbonyl diimine complexes reported in the literatures.

Optical properties

The UV-vis absorption spectra of the free ligand L_R and *R*-1 with the same concentration in CH₂Cl₂ solution were depicted in Fig. 4. The free ligand L_R shows absorption band at 320 nm with extinction coefficient on the order of 10⁴ M⁻¹cm⁻¹ due to the $\pi \rightarrow \pi^*$ transition in L_R . *R*-1 displays intense absorption band at 295 nm with extinction coefficient on the order of 10⁴ M⁻¹cm⁻¹, which can be assigned to spin-allowed intraligand ($\pi \rightarrow \pi^*$) transition. While the low energy broad bands in the 370–650 nm region are attributed to the metal to ligand charge-transfer $d\pi(\text{Re}) \rightarrow \pi^*(L_R)$ (¹MLCT) transition.^{6a} In comparison with mononuclear Re(I) analogues displaying intense emission, It is noteworthy that *R*-1 does not show any detectable emission in the solid state or in the solution. We suggest that the increase of

positive charge owing to the presence of the second metal center lowers the energy levels of the π^* orbitals of the bridging ligand L_R , resulting in the smaller energy gap between $^1\text{MLCT}$ and $^3\text{MLCT}$, which is unfavourable to the emission.¹⁷ The same results also were observed in the similar dinuclear Re(I) complexes with the type of $\text{Cl}(\text{CO})_3\text{Re}(\text{BL})\text{Re}(\text{CO})_3\text{Cl}$ (BL = bridging ligand).^{7i,j,18}

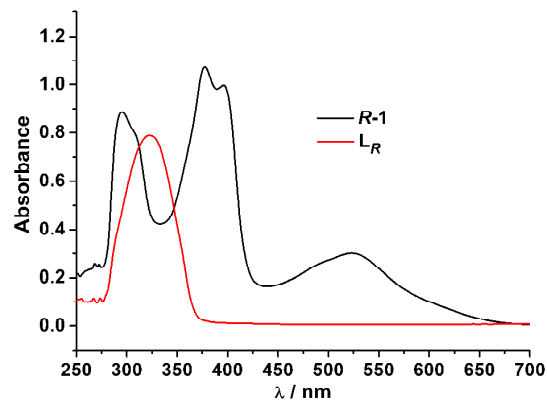


Fig. 4 UV-vis absorption spectra of L_R and $R-1$ in CH_2Cl_2 solution ($1 \times 10^{-5} \text{ mol L}^{-1}$) at room temperature.

Ferroelectric properties

In view of the fact that the chiral space group $P2_1$ of $R-1$ and $S-1$ belongs to the polar point group 2, one of 10 polar point groups (1, 2, 3, 4, 6, m , $mm2$, $3m$, $4mm$ and $6mm$) necessary for the occurrence of ferroelectricity,^{2d} the ferroelectric property of $R-1$ and $S-1$ were examined. The polarization (P)–electric field (E) hysteresis loops of $R-1$ and $S-1$ based on respective single-crystal measurements at room temperature are shown in Fig. 5 and Fig. S2 (in ESI†), respectively. The well-shaped P – E loops obviously indicate their ferroelectric behaviors and the remnant polarization (P_r) value of $R-1$ is $1.6 \mu\text{C}/\text{cm}^2$ at an applied field of $7.3 \text{ kV}/\text{cm}$. The corresponding saturation value of spontaneous polarization (P_s) is $3.1 \mu\text{C}/\text{cm}^2$ for $R-1$. The corresponding parameter values for $S-1$ are very similar to that of $R-1$ (see Fig. S2, ESI†). The P_r value of $R-1$ is comparable with those of dinuclear lanthanide complexes reported by us^{2f,g} and is much larger than that of chiral mononuclear Re(I) tricarbonyl diimine complex $[\text{Re}(\text{CO})_3(\text{L}_{RR})\text{Cl}]$ ($P_r = 0.17 \mu\text{C}/\text{cm}^2$ at an applied field of $4.8 \text{ kV}/\text{cm}$ based on a compressed powder sample).^{6f} The ferroelectricity of $R-1$ may arise from the off-centering of the charges between Re(I) cations and chlorine anions, which results in the spontaneous electric dipolar moments.¹⁹ These dipolar moments are aligned to the same direction (electric domains) under an applied electric field, which lead to the occurrence of ferroelectricity in $R-1$. On the other hand, the remnant polarization (P_r) is correlative to the electric domains. The density of electric domains in $R-1$ is larger than that of mononuclear complex $[\text{Re}(\text{CO})_3(\text{L}_{RR})\text{Cl}]$ because of the increase of charge centers, thus resulting in larger P_r value. Furthermore, it is worthy mentioned that a mononuclear Re(I) complex $[\text{Re}(\text{CO})_3(\text{L}_R)\text{Cl}] \cdot \text{DMF}$, based on the same chiral ligand L_R as that of $R-1$ and ligand-to-metal ratio being 1:1, did not show ferroelectric property due to the fact that it crystallizes in the chiral space group $P2_12_12_1$, belonging to nonpolar point group.²⁰ $R-1$ and $S-1$ not only represent the first example of

polynuclear Re(I) complexes with ferroelectric property but also indicate that the Re nuclearity affects the crystalline polarity and thus the related ferroelectric behavior.

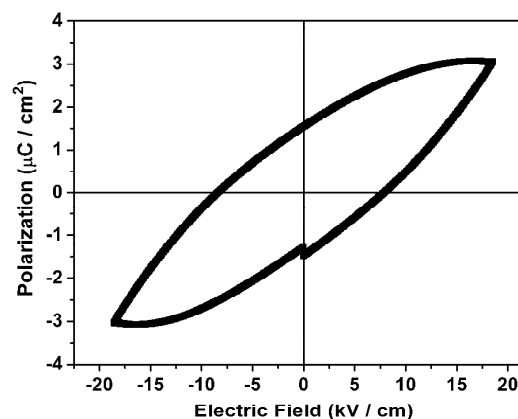


Fig. 5 P – E hysteresis loop of $R-1$ based on a single-crystal sample at room temperature.

Conclusions

In this work, a new dinuclear Re(I) enantiomeric pair ($R-1$ and $S-1$) with the chiral space group $P2_1$ has been successfully prepared based on enantiopure bis-bidentate N-donor ligands. Their chiroptical activities and enantiomeric natures were confirmed by circular dichroism spectra measurements. The investigations on ferroelectric and SHG properties indicated that the homochiral dinuclear Re(I) complexes are potential molecule-based multifunctional materials combining chirality, ferroelectricity and NLO-activity within one molecule. Notably, the ferroelectric properties of chiral dinuclear Re(I) complexes are superior to the chiral mononuclear Re(I) analogue with the identical $P2_1$ space group, representing the first example of polynuclear Re(I) complexes with ferroelectric properties. Furthermore, in comparison with the mononuclear species based on the same chiral ligand L_R , which displays intense emission but shows no ferroelectric property, dinuclear Re(I) enantiomeric pair exhibit obvious ferroelectric behaviors without any emission. So, our research results show that the Re nuclearity has a great influence on not only emitting property but also ferroelectric behaviour, which provides a simple way for modulating emitting and ferroelectric properties of Re(I) complexes by changing the ligand-to-metal ratio (1:1 or 1:2).

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data and additional figures. CCDC 1039529 ($R-1$) and 1039530 ($S-1$). Table of selected bond distances (Å) and angles (°) (Table S1) or other ESI See DOI: 10.1039/b000000x/

- 1 (a) F. L. Lam, F. Y. Kwong and A. S. C. Chan, *Chem. Commun.*, 2010, **46**, 4649; (b) Y. Liu, W. M. Xuan and Y. Cui, *Adv. Mater.*, 2010, **22**, 4112; (c) C. E. Song and S. G. Lee, *Chem. Rev.*, 2002, **102**, 3495; (d) H. K. Ngo and W. Lin, *Top. Catal.*, 2005, **34**, 85; (e) G. C. Fu, *Acc. Chem. Res.*, 2006, **39**, 853.
- 2 (a) S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Piccozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, *Nature*, 2010, **463**, 789; (b) J.-F. Nicoud, *Science*, 1994, **263**, 636; (c) C. Dhenaut, I. Ledoux, I. W. Samuel, J. Zyss, M. Bourgault and H. L. Bozec, *Nature*, 1995, **374**, 339; (d) W. Zhang, H.-Y. Ye and R.-G. Xiong, *Coord. Chem. Rev.*, 2009, **253**, 2980; (e) W. Kaneko, S. Kitagawa and M. Ohba, *J. Am. Chem. Soc.*, 2007, **129**, 248; (f) X.-L. Li, Y.-L. Gao, X.-L. Feng, Y.-X. Zheng, C.-L. Chen, J.-L. Zuo and S.-M. Fang, *Dalton Trans.*, 2012, **41**, 11829; (g) X.-L. Li, C.-L. Chen, Y.-L. Gao, C.-M. Liu, X.-L. Feng, Y.-H. Gui and S.-M. Fang, *Chem. Eur. J.*, 2012, **18**, 14632; (h) X.-L. Li, C.-L. Chen, L.-F. Han, C.-M. Liu, Y. Song, X.-G. Yang and S.-M. Fang, *Dalton Trans.*, 2013, **42**, 5036; (i) K. M. Ok, E. O. Chi and P. S. Halasyamani, *Chem. Soc. Rev.*, 2006, **35**, 710.
- 3 (a) Q. Gao, X. Wang and A. J. Jacobson, *Inorg. Chem.*, 2011, **50**, 9073; (b) Y. Zheng, L.-S. Long, R.-B. Huang and L.-S. Zheng, *Dalton Trans.*, 2012, **41**, 10518; (c) J. Ru, F. Gao, M.-X. Yao, Y.-Z. Li and J.-L. Zuo, *Dalton Trans.*, 2014, **43**, 933; (d) Y.-Y. Yan, Y.-L. Zhao, J.-G. Ma, X.-C. Chao and P. Cheng, *Inorg. Chem.*, 2013, **52**, 3738.
- 4 (a) Z.-B. Han, B.-Y. Li, J.-W. Ji, Y.-E. Du, H.-Y. An and M.-H. Zeng, *Dalton Trans.*, 2011, **40**, 9154; (b) X.-L. Li, L.-F. He, X.-L. Feng, Y. Song, M. Hu, L.-F. Han, X.-J. Zheng, Z.-H. Zhang and S.-M. Fang, *CrystEngComm*, 2011, **13**, 3643; (c) E.-Q. Gao, Y.-F. Yue, S.-Q. Bai, Z. He and C.-H. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 1419; (d) K. K. Bisht and E. Suresh, *J. Am. Chem. Soc.*, 2013, **135**, 15690; (e) X. Tian, J. Zhan, J. Zhang, L. Jiang, M. Pan and C.-Y. Su, *CrystEngComm*, 2012, **14**, 63.
- 5 L. Pérez-García and D. B. Amabilino, *Chem. Soc. Rev.*, 2002, **31**, 342.
- 6 For examples: (a) H.-Y. Li, J. Wu, X.-H. Zuo, L.-C. Kang, D.-P. Li, Y. Sui, Y.-H. Zou, Y.-X. Zheng, J.-L. Zuo and X.-Z. You, *Dalton Trans.*, 2009, 10563; (b) R. Baková, M. Chergui, C. Daniel, A. V. Jr and S. Zláliš, *Coord. Chem. Rev.*, 2011, **255**, 975; (c) Q.-H. Wei, F.-N. Xiao, L.-J. Han, S.-L. Zeng, Y.-N. Duan and G.-N. Chen, *Dalton Trans.*, 2011, **40**, 5078; (d) L. A. Lytwak, J. M. Stanley, M. L. Mejía and B. J. Holliday, *Dalton Trans.*, 2010, **39**, 7692; (e) B.-C. Tzeng, B.-S. Chen, C.-K. Chen, Y.-P. Chang, W.-C. Tzeng, T.-Y. Lin, G.-H. Lee, P.-T. Chou, Y.-J. Fu and A. H. H. Chang, *Inorg. Chem.*, 2011, **50**, 5379; (f) Y.-H. Zhou, J. Li, T. Wu, X.-P. Zhao, Q.-L. Xu, X.-L. Li, M.-B. Yu, L.-L. Wang, P. Sun and Y.-X. Zheng, *Inorg. Chem. Commun.*, 2013, **29**, 18; (g) W. Liu and K. Heinze, *Dalton Trans.*, 2010, **39**, 9554.
- 7 (a) S.-H. Wu, H. D. Abruña and Y.-W. Zhong, *Organometallics*, 2012, **31**, 1161; (b) J. Baiano, D. L. Carlson, G. M. Wolosh, D. E. Dejesus, C. F. Knowles, E. G. Szabo and W. R. Jr. Murphy, *Inorg. Chem.*, 1990, **29**, 2327; (c) W. Kaim and S. Kohlmann, *Inorg. Chem.*, 1990, **29**, 2909; (d) K. Kalyanasundaram and M. K. Marzeeruddin, *J. Chem. Soc. Dalton Trans.*, 1990, 1657; (e) B. J. Yoblinski, M. Stathis and T. F. Guarr, *Inorg. Chem.*, 1992, **31**, 5; (f) S. E. Page, K. C. Gordon, *J. Chem. Soc. Dalton Trans.*, 2002, 1180; (g) M. G. Fraser, C. A. Clark, R. Horvath, S. J. Lind, A. G. Blackman, X.-Z. Sun, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2011, **50**, 6093; (h) S. Roy and C. P. Kubiak, *Dalton Trans.*, 2010, **39**, 10937; (i) K. Parimal, S. Vyas, C.-H. Chen, C. M. Hadad and A. H. Flood, *Inorg. Chim. Acta*, 2011, **374**, 620; (j) G.-N. Li, T. Jin, L. Sun, J. Qin, D. Wen, J.-L. Zuo and X.-Z. You, *J. Organomet. Chem.*, 2011, **696**, 3076; (k) X. Chen, F. J. Femia, J. W. Babich, J. Zubietta, *Inorg. Chim. Acta*, 2001, **315**, 66; (l) T.-P. Lin, C.-Y. Chen, Y.-S. Wen and S.-S. Sun, *Inorg. Chem.*, 2007, **46**, 9201.
- 8 S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 4554.
- 9 S. W. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
- 10 T. Bark, H. Stoekli-Evans and A. V. Zelewsky, *J. Chem. Soc., Perkin Trans. I*, 2002, 1881.
- 11 S. Das and B. K. Panda, *Polyhedron*, 2006, **25**, 2289.
- 12 V. W. W. Yam, V. C. Y. Lau and K. K. Cheung, *Organometallics*, 1995, **14**, 2749.
- 13 D. Wang, Q.-L. Xu, S. Zhang, H.-Y. Li, C.-C. Wang, T.-Y. Li, Y.-M. Jing, W. Huang, Y.-X. Zheng and G. Accorsi, *Dalton Trans.*, 2013, **42**, 2716.
- 14 S. W. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
- 15 D. R. Gamelin, M. W. George, P. Glyn, F.-W. Grevels, F. P. A. Johnson, W. Klotzbüchter, S. L. Morrison, G. Russell, K. Schaffner and J. J. Turner, *Inorg. Chem.*, 1994, **33**, 3246.
- 16 M. V. Werrett, D. Chartrand, J. D. Gale, G. S. Hanan, J. G. Maclellan, M. Massi, S. Muzzioli, P. Raiteri, B. W. Skelton, M. Silberstein and S. Stagni, *Inorg. Chem.*, 2011, **50**, 1229.
- 17 (a) R. Sahai, D. P. Rillema, R. Shaver, S. V. Vallendael, D. C. Jackman and M. Boldaji, *Inorg. Chem.*, 1989, **22**, 1022; (b) J. R. Kirchoff and K. Kirschbaum, *Polyhedron*, 1998, **17**, 4033.
- 18 A. Vogler and Kisslinger, *Inorg. Chim. Acta*, 1986, **115**, 193.
- 19 F.-H. Zhao, Y.-X. Che, J.-M. Zheng and F. Grandjean, *Inorg. Chem.*, 2012, **51**, 4862.
- 20 S.-J. Li, X.-P. Zhang, J. Liu, W. Zheng and C.-H. Li, *Chin. J. Inorg. Chem.*, 2013, **29**, 1745.

Table 1. X-ray crystallographic data for complexes R-1 and S-1

	R-1	S-1
Chemical formula	C ₃₈ H ₃₈ N ₄ O ₆ Cl ₁₀ Re ₂	C ₃₈ H ₃₈ N ₄ O ₆ Cl ₁₀ Re ₂
Formula weight	1373.62	1373.62
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁	P2 ₁
a/Å	11.6966(7)	11.6986(3)
b/Å	10.4541(4)	10.4365(3)
c/Å	19.4795(15)	19.3757(6)
β°	93.697(6)	93.659(3)
V/Å ³	2376.9(2)	2360.80(12)
Z	2	2
D/g cm ⁻³	1.919	1.932
μ/mm ⁻¹	5.698	5.737
GOF	1.069	1.029
R ₁ ^a /wR ₂ ^b	0.0725/0.1888	0.0522/0.1355
Flack parameter	0.01(3)	0.02(3)

$$10^5 \text{ } ^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \text{ } ^b wR_2 = \left[\frac{\sum W(F_o^2 - F_c^2)^2}{\sum W(F_o^2)^2} \right]^{1/2}$$

A pair of dinuclear Re(I) enantiomers: synthesis, crystal structures, chiroptical and ferroelectric properties†

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A pair of dinuclear Re(I) enantiomers have been successfully synthesized, representing the first example of polynuclear Re(I) complexes with ferroelectric property and possessing a multifunctional feature combining chirality, NLO-activity and ferroelectricity within one molecule.

