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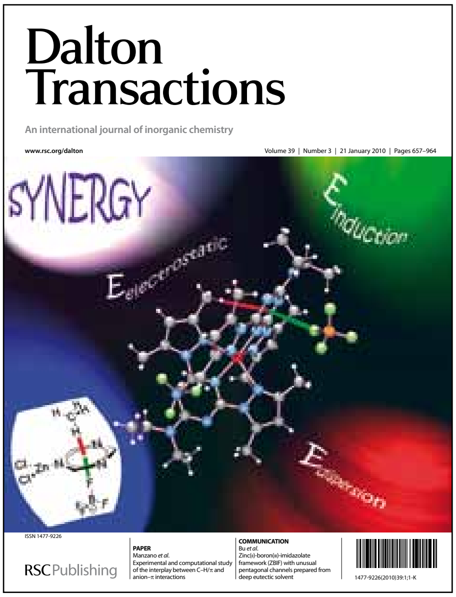

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ARTICLE TYPE

Butterfly-like enantiomerically homochiral $\{Co^{II}_6Co^{III}_4\}$ clusters exhibiting both slow magnetic relaxation and ferroelectric property

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A pair of enantiomerically homochiral $\{Co^{II}_6Co^{III}_4\}$ clusters featuring a butterfly-like structure, formulated as $[Co^{II}_6Co^{III}_4(\mu_3\text{-OH})(\mu_3\text{-X})(S\text{-pa})_4(pdm)_6(pdmH)_2](ClO_4)_4\cdot 3.5H_2O$ (***S*-1**) and $[Co^{II}_6Co^{III}_4(\mu_3\text{-OH})(\mu_3\text{-X})(R\text{-pa})_4(pdm)_6(pdmH)_2](ClO_4)_4\cdot 3.5H_2O$ (***R*-1**) (X = OH or OMe, *S*- or *R*- paH = *S*- or *R*-phenylalaninol and $pdmH_2$ = pyridine-2,6-diyldimethanol), have been synthesized and structurally characterized. They are the second largest homochiral Co clusters constructed by chiral ligands. They are also the first example of high-nuclearity homochiral Co clusters having both slow magnetic relaxation behaviour and ferroelectric property.

Introduction

The synthesis of high-nuclearity transition-metal clusters remains a research focus owing to their aesthetical structures and rich electronic and magnetic properties.[1] To date, much effort has been devoted to the design and synthesis of chiral high-nuclearity cluster complexes as chirality can induce novel functions such as magnetochiral dichroism (MChD) effect,[2] nonlinear optical[3] and ferroelectric properties[4] in the magnetic molecules, generating multifunctional molecular materials. Unfortunately, up to now, only a few of them with the nuclearities higher than ten have been synthesized and structurally characterized because the chances of getting chiral cluster complexes are very low[5] and the preparation of them usually requires suitable enantiomerically pure chiral ligands.[6] Although several large-sized chiral polynuclear metal cluster complexes constructed by lanthanide,[7] Mn,[8] Fe[9] and Ni[10] ions and various chiral ligands have been reported, those with Co ions are extremely rare. In fact, there has been only one chiral Co cluster with more than ten metals, i.e. $[Co^{II}_{16}(L)_4(H_3L)_8(N_3)_6](NO_3)_2\cdot 16H_2O\cdot 2CH_3OH$ (H_4L = *S*, *S*-1,2-bis(1*H*-benzimidazol-2-yl)-1,2-ethanediol), which is also the biggest chiral cobalt cluster known so far.[11] Besides, among the chiral high-nuclearity clusters, only one complex with a Mn_{25} core has been reported to exhibit ferroelectric properties.[8e] The difficulty to make high-nuclearity chiral clusters with ferroelectric properties is that they must also crystallize in the ten polar point groups required for ferroelectric materials.[4]

By utilizing a mixed ligand system of enantiomeric *S*- or *R*-paH (paH = phenylalaninol) (Fig. 2a) and $pdmH_2$ (pyridine-2,6-diyldimethanol), we successfully work out the formation of two enantiomorphic mixed-valence Co_{10} cluster complexes, namely $[Co^{II}_6Co^{III}_4(\mu_3\text{-OH})(\mu_3\text{-X})(S\text{-pa})_4(pdm)_6(pdmH)_2](ClO_4)_4\cdot 3.5H_2O$ (***S*-1**) and $[Co^{II}_6Co^{III}_4(\mu_3\text{-OH})(\mu_3\text{-X})(R\text{-pa})_4(pdm)_6(pdmH)_2](ClO_4)_4\cdot 3.5H_2O$ (***R*-1**) (X = OH or OMe). To the best of our knowledge, they are the second largest homochiral cobalt clusters based on the homochiral ligands.[11] Furthermore they are also the first example of high-nuclearity homochiral cobalt clusters, which exhibit both slow magnetic relaxation behaviour and ferroelectric property.

Experimental

Materials and methods

All the chemicals were purchased commercially and used as received. Caution! Perchlorate salts are potentially hazardous and caution should be exercised when dealing with such salts.

Synthesis of $[Co^{II}_6Co^{III}_4(\mu_3\text{-OH})(\mu_3\text{-X})(S\text{-pa})_4(pdm)_6(pdmH)_2](ClO_4)_4\cdot 3.5H_2O$ (*S*-1) and $[Co^{II}_6Co^{III}_4(\mu_3\text{-OH})(\mu_3\text{-X})(R\text{-pa})_4(pdm)_6(pdmH)_2](ClO_4)_4\cdot 3.5H_2O$ (*R*-1) (X = OH or OMe).

A mixture of $Co(ClO_4)_2\cdot 6H_2O$ (733 mg, 2.00 mmol), $NaAc\cdot 3H_2O$ (136 mg, 1.00 mmol), *S*-paH (151 mg, 1.00 mmol) and $pdmH_2$ (139 mg, 1.00 mmol) were dissolved in 20 mL of MeOH / MeCN (1 : 1, v / v). The mixture was stirred at room temperature for a few minutes and then excess Et_3N (2 mL) was added under vigorous stirring, which caused a rapid colour change from pink to red brown. The solution was stirred for another 3 h, then the resulting dark brown solution was filtered and the filtrate left undisturbed at ambient temperature. After several days, the red-brown prism crystals of ***S*-1** was obtained by filtration, washed with MeOH (2 × 5 mL) and dried under vacuum. The yield is 45% based on cobalt. Anal. calcd for $C_{92.5}H_{109}Co_{10}N_{12}O_{22}\cdot 4(ClO_4)\cdot 3.5(H_2O)$ (***S*-1**): C 39.81, H 4.19, N 6.02. Found: C 39.49, H 4.33, N 5.94. IR (KBr, cm^{-1}): 3434 s, 1592 v, 1584 m, 1448 m, 1120 s, 1092 s, 780 vw, 706 vw, 638 w, 532 vw.

R*-1** was prepared in a way similar to that for ***S*-1** except that *R*-paH was used instead of *S*-paH (yield 58% based on cobalt). Anal. calcd for $C_{92.5}H_{109}Co_{10}N_{12}O_{22}\cdot4(ClO_4)\cdot3.5(H_2O)$ (R*-1**): C 39.81, H 4.19, N 6.02. Found: C 39.72, H 4.30, N 5.83. IR (KBr, cm^{-1}): 3436 s, 1600 m, 1591 m, 1445 m, 1120 s, 1092 s, 782 vw, 752 vw, 702 w, 626 w, 526 vw.

X-ray Crystallography

Single-crystal X-ray diffraction data were collected on a Rigaku diffractometer with a MM007 CCD area detector (Mo Kα; λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied to the data using the *CrystalClear* program.[12] The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the *SHELXTL-97* program.[13] Metal atoms in both complexes were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically except those of guest water molecules. The disorder of perchlorates, one of the hydroxide ions and some lattice water molecules has been treated and the detailed process is added in the Supporting Information.

Crystal data

$C_{92.5}H_{109}Co_{10}N_{12}O_{22}\cdot4(ClO_4)\cdot3.5(H_2O)$ (***S*-1**): M = 2791.07, monoclinic, a = 15.033(7), b = 25.599(11), c = 15.034(7) Å, β = 107.686(7)º, V = 5512(4) Å^3, space group $P2_1$, Z = 2, D_{calc} = 1.682 g cm^{-3}, μ = 1.652 mm^{-1}, 44192 reflections measured, 24255 unique (R_{int} = 0.0362), 20344 reflections with $I > 2\sigma(I)$, 1626 parameters refined, R_1 = 0.0541, wR_2 = 0.1353, GOF = 1.006, CCDC reference number 950149.

$C_{92.5}H_{109}Co_{10}N_{12}O_{22}\cdot4(ClO_4)\cdot3.5(H_2O)$ (***R*-1**): M = 2791.07, monoclinic, a = 15.130(8), b = 25.739(12), c = 15.205(7) Å, β = 107.966(9)º, V = 5633(5) Å^3, space group $P2_1$, Z = 2, D_{calc} = 1.646 g cm^{-3}, μ = 1.617 mm^{-1}, 35399 reflections measured, 18670 unique (R_{int} = 0.0659), 9205 reflections with $I > 2\sigma(I)$, 1551 parameters refined, R_1 = 0.0647, wR_2 = 0.1306, GOF = 1.004, CCDC reference number 950150.

Physical measurements

Thermogravimetric analysis (TGA) was performed using a TGA/NETZSCH STA449C instrument heated from 30–1000 ºC (heating rate of 10 ºC/min, nitrogen stream). The powder X-ray diffraction (PXRD) patterns were recorded on a PAN alytical X'pert PRO X-Ray Diffractometer on crushed single crystals in the 2θ range 5–50º using Cu-Kα radiation. The IR spectra using the KBr pellet technique were recorded on a Spectrum-One FT-IR spectrophotometer. Elemental analyses (C, H and N) were measured with an Elemental Vairo EL III Analyzer. The solid-state CD spectra were carried out using a mixture of compounds and dried KCl powder, which was well grounded and then pressed into a disk for use in the CD measurement with a MOS-450 spectropolarimeter.

Magnetic and ferroelectric measurements

Magnetic susceptibility data were collected on a Quantum Design MPMS (SQUID)-XL magnetometer and a PPMS-9T system. The sample of ***S*-1** was dried under vacuum at room temperature for several hours before measurements. The sample was measured in a gel capsule using n-eicosane to restrain the crystallites from moving.

The ferroelectric measurements were performed on a pressed powder pellet, which is deposited with silver conducting glue. The ferroelectric hysteresis loops were examined at room temperature by an aix-ACCT TF2000 analyzer (at f = 1 Hz) combined with a high-voltage supply amplifier/controller (Trek, model 610E). The temperature dependence of the dielectric constant and the dielectric loss were measured with a computer-controlled Alpha-A broadband dielectric/impedance spectrometer (Novocontrol GmbH) with an AC signal of 1.0 V (peak-to-peak) applied.

Results and discussion

Synthesis

Among the numerous ligands used to construct multinuclear metal clusters, pyridine derived alcohols are simple but powerful tools because of their simultaneous *O*, *N* chelating and *O*-bridging capabilities.[16b] In particular, $pdmH_2$ is a good chelating and bridging ligand that can foster the formation of polynuclear clusters. The combined use of $pdmH_2$ and chiral alkamine ligands may be a promising approach to synthesize homochiral high nuclearity clusters. Thus, the 1:1:2:1 reaction of enantiomeric *S*- or *R*-paH, $pdmH_2$, $Co(ClO_4)_2\cdot6H_2O$ and $NaAc\cdot3H_2O$ with a mixed solvent of MeOH and MeCN in the presence of excess Et_3N resulted in a red-brown solution from which ***S*-1** or ***R*-1** was isolated in moderate yield. Although the Ac^- anion was not found in the structures of the final products, it is necessary to the formation of complexes ***S*-1** and ***R*-1**. In the absence of $NaAc\cdot3H_2O$, complexes ***S*-1** and ***R*-1** could not be obtained as immediate precipitation happened upon the addition of Et_3N.

Description of crystal structures

Single crystal X-ray structural analyses show that ***S*-1** and ***R*-1** both crystallize in the chiral space group of $P2_1$ with the Flack parameters of -0.0041 and 0.0159, respectively, indicating the enantiomeric purity of the single crystal (Table S1†). Because the structure of ***R*-1** (Fig. S4†) is essentially the same as that of ***S*-1**, only the structure of ***S*-1** is discussed in detail.

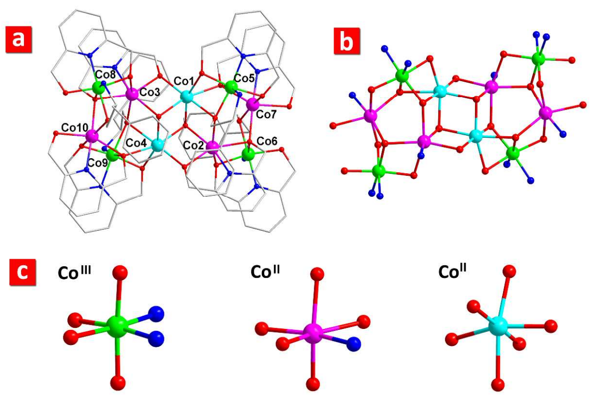

Fig. 1 (a) The butterfly-like structure of ***S*-1**. (b) The core structure of the $\{Co^{II}_6Co^{III}_4\}$ cluster. (c) The coordination mode of the Co^{III} ion (green) and two different kinds of coordination modes for Co^{II} ions (pink and turquiose) in ***S*-1**. Oxygen (red), nitrogen (blue).

The asymmetric unit of **_S_-1** contains ten crystallographically independent cobalt ions, four *S*-pa$^-$, two pdmH$^-$, six pdm^{2-}, one μ_3-OH$^-$ and one μ_3-X$^-$ (X = OH or OMe) ligands, four ClO_4^- anions and three and a half lattice water molecules (Fig. 1a). The X group in both complexes are disordered which can be split by half OH$^-$ and half OMe$^-$. The Co–O/N bond distances and Co–O/N–Co angles, ranging from 1.848(6) to 2.289(4) Å and 72.70(16) to 156.96(17)º, respectively, are normal for this type of cluster complexes (Table S2†). Based on the bond valence sum (BVS) calculations,[14] Co5, Co6, Co8 and Co9 are assigned the oxidation state of +3, whereas Co1, Co2, Co3, Co4, Co7 and Co10 are assigned the oxidation state of +2 (Table S3†). The ten Co ions in **_S_-1** are in an approximately octahedral geometry with different coordination environments (Fig. 1c). The Co(III) ions each adopts a CoN2O4 configuration, tris-chelated by one pdm^{2-} ligand, chelated by one *S*-pa$^-$ ligand and bonded to one O atom from another pdm^{2-}. One type of Co(II) ions adopt a CoNO5 configuration: Co2 and Co3 are tris-chelated by one pdm^{2-} ligand, coordinated by one O atom from another pdm^{2-} ligand and one O atom from a *S*-pa$^-$ ligand, and bonded to one μ_3-OH$^-$/OMe$^-$ (for Co2) or one μ_3-OH$^-$ (for Co3) oxygen atom, while Co7 and Co10 are tris-chelated by one pdmH$^-$ ligand, coordinated by two O atoms from two different pdm^{2-} ligands and one O atom from a *S*-pa$^-$ ligand. The other type of Co(II) ions (Co1 and Co4) have a CoO6 sphere completed by one μ_3-OH$^-$ anion and one μ_3-OH$^-$/OMe$^-$ anion, and four oxygen atoms from two different pdm^{2-} ligands, a pdmH$^-$ ligand and a *S*-pa$^-$ ligand, respectively. Two of the four *S*-pa$^-$ ligands adopt a [2.21] coordination mode, while the other two have a [3.31] coordination mode. The pdmH$_2$ ligands adopt [4.321] and [2.211] coordination modes (Scheme S1†). The μ_3-OH$^-$ anion connects to Co1, Co3 and Co4 ions while the μ_3-OH$^-$/OMe$^-$ bridge links to Co1, Co2 and Co4 ions. The metal core of **_S_-1** can be considered as a fusion of eight edge-sharing triangles, with the distances of adjacent Co atoms varying from 2.730 to 3.800 Å (Fig. 1b). It is interesting to note that **_S_-1** features a butterfly-like geometry that has rarely observed for cobalt cluster complexes (Fig. 1a).[15] The Co$_{10}$ clusters are further linked by hydrogen bonding, resulting in a 3D supramolecular architecture with left-handed helixes (Fig. S5†).

Solid-state circular dichroism spectrums

Solid-state circular dichroism (CD) spectra of **_S_-1** and **_R_-1** are measured in KCl pellet to observe the absolute configurations and optical activity of the enantiomers. Complex **_S_-1** exhibits a strong negative Cotton effect at 508 nm, two negative dichroic signals centered at 331 and 571 nm and a positive Cotton effect at 428 nm, while **_R_-1** shows Cotton effects with opposite signals at the same wavelengths as **_S_-1** (Fig. 2b). This result is in agreement with the structures obtained by single crystal X-ray diffraction analysis.

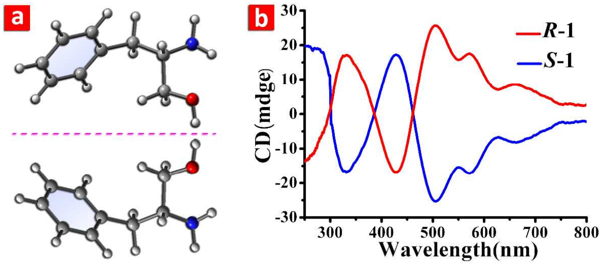

Fig. 2 (a) Chiral *R*- and *S*-paH ligands (up and down). (b) The solid-state CD spectra of **_R_-1** and **_S_-1**.

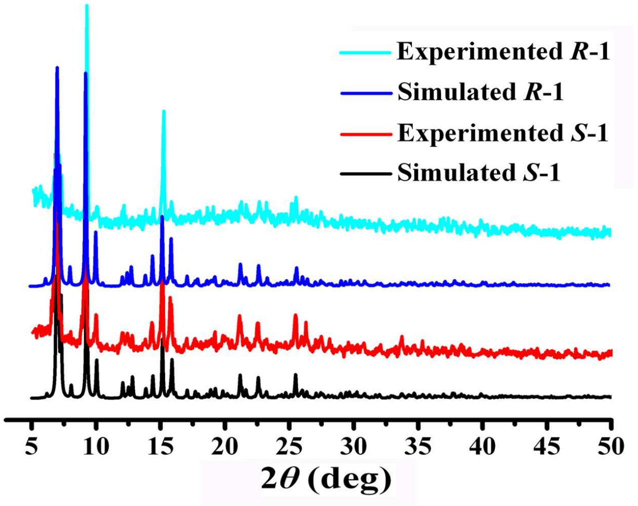

Fig. 3 Simulated and experimental XRD powder patterns of **_S_-1** and **_R_-1**.

X-ray diffraction and thermal stability analysis

The powder X-ray diffractions (PXRD) are performed to test the purity of **_S_-1** and **_R_-1** (Fig. 3). The experimental results match well with the simulated XRD patterns, indicating the phase purity of the as-synthesized samples. Thermogravimetric analysis (TGA) measurements are conducted in the temperature range of 30–1000°C under a flow of nitrogen with the heating rate of 10°C min^{-1}. The TGA curve of **_S_-1** indicates that the first step from 40 to 200°C with a weight loss of 2.31% is due to the loss of 3.5 lattice water molecules (calcd 2.26%), and then it begins to decompose upon further heating. The TGA curve of **_R_-1** is very similar to that of **_S_-1** (Fig. S6†).

Magnetic property

The dc magnetic susceptibility measurement is performed on the crystalline sample of **_S_-1** in the temperature range of 300-2 K at the field of 1000 Oe. The $x_{\rm m}T$ value of **_S_-1** at room temperature is 18.02 cm^3 K mol^{-1}, which is significantly larger than the spin-only value of six high-spin Co(II) ions (11.25 cm^3 K mol^{-1}).[16] This is a common phenomenon for Co(II) complexes because of the significant orbital contributions of the distorted octahedral Co(II) ions.[17] Upon lowering the temperature, the $x_{\rm m}T$ value decreases continuously and reaches a minimum of 13.15 cm^3 K mol^{-1} at 18.39 K. Below 18.39 K, the $x_{\rm m}T$ increases slightly to a value of 14.65 cm^3 K mol^{-1} at 3.96 K and then falls rapidly to 13.06 after cooling to 2 K (Fig. 4a). In the range of 300 to 18.39 K, the decrease is mainly due to the single ions effect of Co(II), and the information about the contributions of exchange interactions to the temperature-dependent behavior is impossible to obtain. Below 18.39 K, the ferromagnetic coupling between the effective spins S_i' of Co(II) ions overcomes the effect of spin-orbital coupling and compensates the decrease of $x_{\rm m}T$, leading to a sharp increase of $x_{\rm m}T$.

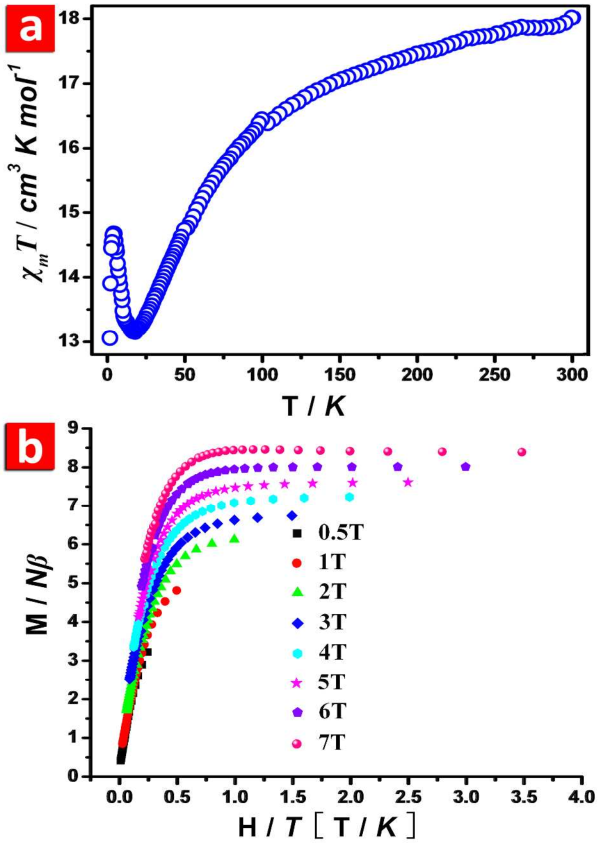

Fig. 4 (a) The plots of $x_{m}T$ *vs*. *T* for ***S*-1**. (b) Plots of reduced magnetization (*M*/*Nβ*) *vs*. *H*/*T* in the ranges 2–30 K and 0.1–7 T of ***S*-1.**

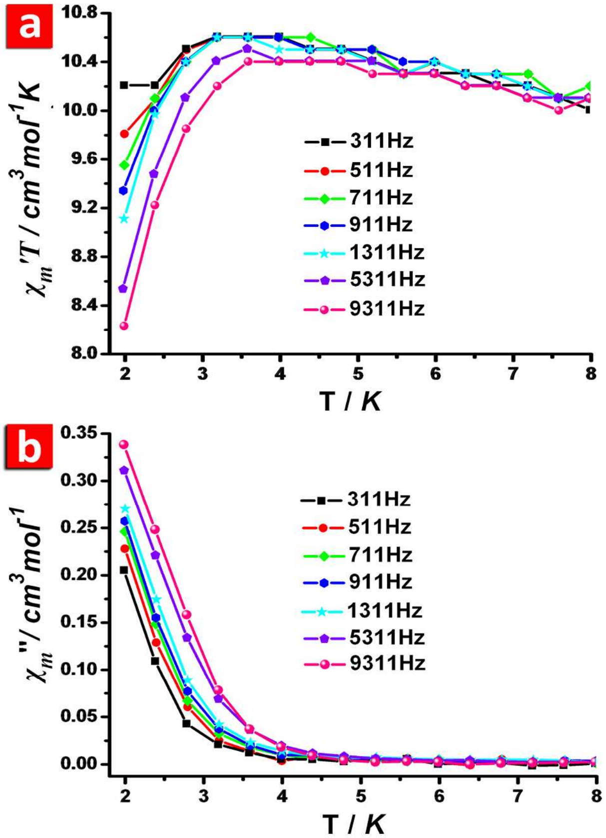

Fig. 5 Ac susceptibility measured in zero dc fields and plotted as $\chi_m'T$ *vs*. T (a) and χ_m'' *vs*. T (b) for ***S*-1**.

In order to determine the spin ground state for ***S*-1**, the field dependence of magnetization in different magnetic fields (0.5–7 T) are collected in the temperature range 2–30 K and are plotted as reduced magnetization (*M*/*Nβ*) *vs H*/*T* (Fig. 4b). These data show that saturation occurs at a value lower than 8.40 *Nβ* and the various isofield lines do not superimpose, indicating the presence of low-lying excited states in strong magnetic field.[16] Further evidence can be observed in variable-field magnetization curve in Fig. S7†, where the magnetization increases rapidly with the increase of the magnetic field, and does not reach saturation even at $H = 7$ T.[17d]

To characterize the low-temperature behaviour of ***S*-1**, the temperature dependencies of field-cooled (FC) and zero-field cooled (ZFC) magnetization were performed under a field of 50 and 100 Oe (Fig. S8†). The FC curves are consistent with the ZFC curves, and the magnetizations increase continuously with decreasing temperature. Besides, no bifurcation points were observed. These results indicate the absence of any long-range magnetic ordering in ***S*-1**.

To further investigate whether ***S*-1** could be a candidate of single molecule magnet (SMM), ac susceptibility measurements are carried out in zero-applied dc field with a 3 Oe ac field oscillating at the indicated frequencies (311–9311Hz) under the temperature range of 2-8 K (Fig. 5). Both the in-phase and out-of-phase signals display frequency dependence below 8 K, suggesting that ***S*-1** may be a SMM.[18]

Ferroelectric property

Because ***S*-1** crystallizes in the chiral space group $P2_1$, which falls into the ten polar points (C_1, C_s, C_2, C_{2v}, C_3, C_{3v}, C_4, C_{4v}, C_6 and C_{6v}), it may have potential ferroelectric property.[4] The ferroelectric behaviour of ***S*-1** is observed for a pressed powder pellet sample using a ferroelectric tester at room temperature. It clearly shows that there is an electric hysteresis loop with a remnant polarization (*P*r) of 0.0146 μC cm^{-2}, coercive field (*E*c) of 864.51 V cm^{-2} and the saturation value of the spontaneous polarization (*P*s) of 0.0343 μC cm^{-2} (Fig. 6a).

The temperature dependence of permittivity $(\varepsilon) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$ of ***S*-1** is also investigated from 0 to 100ºC at various frequencies between 1 and 10^4 Hz, where the $\varepsilon_1(\omega)$ and $i\varepsilon_2(\omega)$ represent the real (dielectric constant) (Fig. 6b) and imaginary (dielectric loss) parts (Fig. S9†), respectively. As can be seen from Fig. 6b, the frequency dielectric constant is strongly temperature-dependent: it increases continuously and ascends rapidly for $T > 20$ °C upon warming, reaching a value of 208.9 at 1 Hz and 100 °C, confirming the ferroelectric property.[8e]

Conclusion

In summary, we have reported two novel enantiomorphic $\{Co^{II}_6Co^{III}_4\}$ cluster complexes with butterfly-like architectures, which are the second largest homochiral cobalt clusters based on

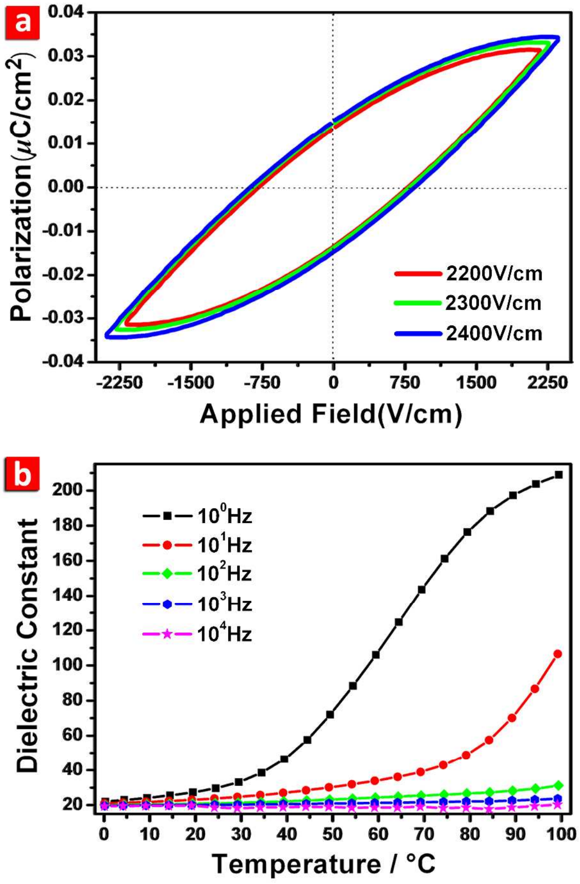

Fig. 6 (a) Electric hysteresis loop for ***S*-1** at room temperature, observed for a pressed powder pellet sample using a ferroelectric tester. (b) The temperature dependence of the dielectric constant of ***S*-1** at various frequencies between 1 and 10^4 Hz.

the chiral ligands. In addition, they are also the first example of high-nuclearity homochiral cobalt clusters that exhibit both slow magnetic relaxation behaviour and ferroelectric property. This work shows that the combined use of enantiomerically pure chiral alkamine and pyridine-alcoholate ligands may provide a useful and promising approach to synthesize homochiral high nuclearity multifunctional molecule-based materials.

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†Electronic Supplementary Information (ESI) available: Synthesis, X-ray crystallographic analysis, additional figures, IR, TGA and XRD pattern. CCDC: 950149 (***S*-1**) and 950150 (***R*-1**). For ESI and crystallographic data in CIF or other electronnic format see DOI: 10.1039/b000000x/.

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Graphical Abstract

A pair of butterfly-like enantiomerically homochiral [$Co^{II}_6Co^{III}_4$] clusters with both slow magnetic relaxation behaviour and ferroelectric property was synthesized.