

Spontaneous resolution of a novel chiral coordination polymer through supramolecular interactions and solvent symmetry breaking

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Abstract—The spontaneous resolution reaction of racemic *trans*-2,3-dihydro-2,3-dipyridyl-benzo[*e*]indole **1** with $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of 2-butanol under solvothermal reaction conditions favors the formation of crystal **2** [P - $\text{Cd}(\text{R},\text{R},\text{-1})_2(\text{ClO}_4)_2$], while a similar reaction in the presence of ethanol only favors the formation of crystal **3** [M - $\text{Cd}(\text{S},\text{S},\text{-1})_2(\text{ClO}_4)_2$]. The crystal structural determination shows that both **2** and **3** crystallize in chiral enantiomorphous space groups ($P6_122$ and $P6_522$) and their structures are 1D infinite chain, and are just enantiomorphous pairs most like. The spontaneous resolution process displays estimated ee values of ca. +0.6 for 2-butanol and ca. –0.4 for ethanol. Enantiomerically pure (S,S)-*trans*-2,3-dihydro-2,3-dipyridyl-benzo[*e*]indole (S,S -**1**) can be obtained through the decomposition of mechanically separated **3**. Additionally (S,S -**1**) also crystallizes in a chiral space group ($P2_1$). The CD (circular dichroism) spectra of both **2** and **3** in the solid state are also approximately enantiomorphous pairs. However, their fluorescent spectra in the solid state display a moderate difference in maximum emission peaks ($\Delta\lambda = 19$ nm). Crystal data for **2**: $\text{C}_{44}\text{H}_{34}\text{Cl}_2\text{N}_6\text{O}_8\text{Cd}$, $M = 958.07$, hexagonal, $P6_122$, $a = 10.5488(5)$, $c = 68.256(4)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 120^\circ$, $V = 6577.8(6)$ Å³, $Z = 6$, $D_c = 1.451$ mg m⁻³, $R_1 = 0.0498$, $wR_2 = 0.1124$, $\mu = 0.679$ mm⁻¹, $S = 0.623$, Flack $\chi = -0.02(6)$. For space group $P6_522$, $R_1 = 0.0670$, $wR_2 = 0.1602$, $S = 0.725$ with a Flack value of 1.03(7); Crystal data for **3**, $\text{C}_{44}\text{H}_{34}\text{Cl}_2\text{N}_6\text{O}_8\text{Cd}$, $M = 958.07$, hexagonal, $P6_522$, $a = 10.5446(3)$, $c = 68.265(3)$ Å, $V = 6573.3(4)$ Å³, $Z = 6$, $D_c = 1.452$ mg m⁻³, $R_1 = 0.0444$, $wR_2 = 0.1002$, $\mu = 0.679$ mm⁻¹, $S = 0.558$, Flack $\chi = 0.01(5)$. For space group $P6_122$, $R_1 = 0.0501$, $wR_2 = 0.1178$, $S = 0.599$ with a Flack value of 1.00(5). The low Flack parameter indicates that the absolute configurations of **2** and **3** are stated; Crystal data for (S,S)-**1**, $\text{C}_{22}\text{H}_{17}\text{N}_2$, $M = 323.39$, orthorhombic, $P2_12_12_1$, $a = 9.2598(7)$, $b = 9.4617(8)$, $c = 19.1452(16)$ Å, $V = 1677.4(2)$ Å³, $Z = 4$, $D_c = 1.281$ mg m⁻³, $R_1 = 0.0417$, $wR_2 = 0.1191$, $T = 293$ K, $\mu = 0.077$ mm⁻¹, $S = 0.862$.

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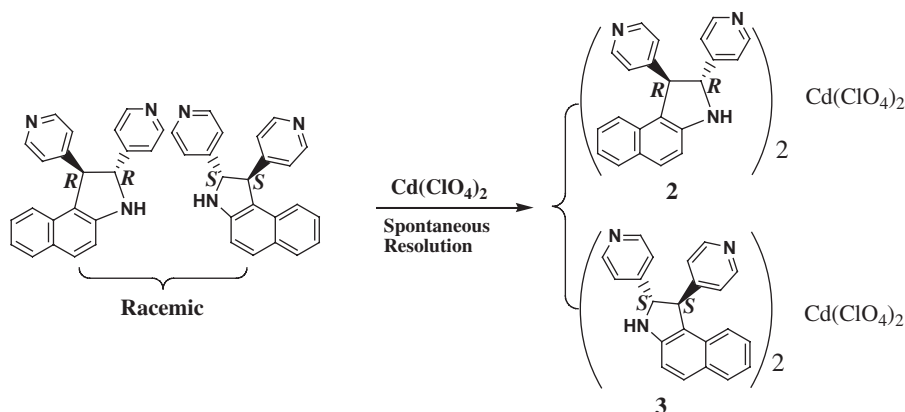
1. Introduction

The noncovalent coordination chemistry of metal complexes at a supramolecular level provides an efficient approach to generating chiral coordination polymers. Such strategies are currently receiving a considerable amount of attention in view of their potential applications in enantioselective synthesis, asymmetric catalysis, porous materials, nonlinear optical materials and magnetic materials.^{1,2} Indeed, methodologies such as the homochiral crystallization of achiral materials, for example, have been shown to be useful and efficient protocols for obtaining individual enantiomeric chiral crystals.³ However, since the discovery of spontaneous resolution

in 1848 by Louis Pasteur,⁴ it remains a challenge to realize the isolation of such bulky enantiomeric chiral crystalline materials from starting substrates, which is not dependant on the homochiral component.

Recently, conglomerate crystallization processes arising from a rapidly racemizing solution (molten state) or mechanical stirring have been reported to give high enantiomeric excess (ee).^{5,6} Conglomerate crystallization is often referred to as total spontaneous resolution and is a chiral symmetry breaking transition. It is postulated to involve the enhancement of secondary nucleation, which results in the cloning of crystals with the same chirality leading to subsequent chiral symmetry breaking transition from the action of mechanical stirring or molten state. The molten state of 1,1-binaphthyl and the mechanically stirred crystallization of NaClO_3 from its aqueous solution are two typical chiral breaking

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Scheme 1.

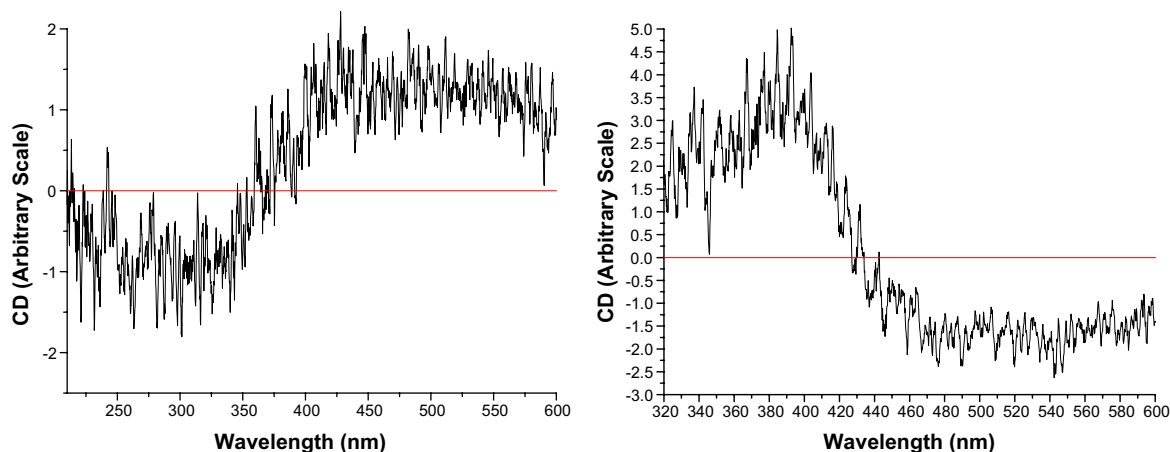
examples of crystallization by ‘external influences or measures’ to effect the resolution of racemates. In view of such precedent, we were intrigued to carry out a study of a novel chiral coordination polymer derived from racemic *trans*-2,3-dihydro-2,3-dipyridyl-benzo[*e*]indole **1** and Cd(ClO₄)₂·6H₂O. Herein, we report the one-pot synthesis of Cd(**1**)₂(ClO₄)₂ under different solvothermal conditions, which undergoes self-resolution to give the two *P*- and *M*-enantiomorphous crystalline forms *P*-Cd(*R,R*-**1**)₂(ClO₄)₂ **2** and *M*-Cd(*S,S*-**1**)₂(ClO₄)₂ **3** and, in the course of this work, the isolation and structural characterization of these enantiomorphous pair crystals by X-ray crystallography and a study on their optical properties (Scheme 1). To our knowledge, the present study is so far the only example of a synthetic approach capable of furnishing enantiomorphous pair crystals, which have been isolated and structurally characterized by X-ray crystallography. The present study should facilitate understanding the spontaneous resolution mechanism through supramolecular crystal engineering and metal coordination effect.

2. Results and discussion

Racemic *trans*-2,3-dihydro-2,3-dipyridyl-benzo[*e*]indole **1** was prepared from the molten reaction of 2-naphthol,

4-(aminomethyl)pyridine and 4-pyridinecarboxaldehyde at about 180 °C following a procedure previously developed in our laboratory.⁷ Block crystals with an approximate dimension of 0.40 × 0.25 × 0.20 mm of **2** were furnished under solvothermal reaction conditions while a block those of **3** with an approximate dimension of 0.35 × 0.20 × 0.20 mm were obtained under solvothermal reaction conditions. Their IR spectra show that there are two strong peaks at 1125 and 1038 cm⁻¹ for **2**, and 1123 and 1036 cm⁻¹ for **3**, respectively, suggesting the presence of a perchlorate ion existing in them.

By defining ee as equal to $(\#d - \#l)/(\#d + \#l)$, where $\#d$ and $\#l$ are the numbers of *d* and *l* crystals formed in a given experiment, respectively, all *d* crystals are expected to give an ee value = +1 and all *l* crystals are expected to give an ee value = -1. For the above mentioned compounds, ee values of ca. +0.6 have been estimated for 2-butanol and ca. -0.4 for ethanol. As shown in Figure 1, the observed circular dichroism (CD) spectra for both alcohols in the solid state reveal an enantiomorphous pair spectrum. The chiral crystals of **2** exhibit a CD spectrum with an exciton-coupled split positive Cotton effect (Fig. 1a) for the absolute helicity *P* (clockwise), as discussed later in the case of the crystal structure depicted in Figure 3 showing a positive to negative effect on going from longer to shorter wave-

Figure 1. CD spectra of **2** and **3** in the solid state.

lengths. For **3**, the opposite was found with an exciton-coupled split negative Cotton effect observed, as shown in Figure 1b for the absolute helicity *M* (counterclockwise) (also see Fig. 3). Remarkably, the crystallization of **2** and **3** are homochiral and all the crystals (pale yellow blocks 1–10 mm long) recovered from a single crystallization found to have the same CD sign, which suggests the same chirality (helicity). In fact, crystals of **2** and **3** were observed to grow radially as a single colony from the first-appearing nucleus and it is presumably for this reason that we find the preservation of a single chirality during the crystal growth process. In this way, racemic 2-butanol and ethanol solvents can induce two enantiomerically pure chiral coordination polymers **2** and **3** simply upon metal coordination and crystallization. This phenomenon is unprecedented in coordination polymers. However, the spontaneous resolution of the racemic organic compounds in different solvents displays different ees.⁸ Moreover, the conditions required for resolving racemates into enantiomers by crystallization involve a deficiency of either the conglomerator or the achiral solubilizer to promote the solubility of the compound to be resolved.⁸ For the present case, the nucleation velocity of the formation of crystal **2** in 2-butanol solvent may be slightly faster than that of the formation of crystal **3**. Conversely, the nucleation velocity of the formation of crystal **2** in the ethanol solvent should be slightly slower than that of the formation of crystal **3**. Thus, the spontaneous resolution reaction of **1** with Cd(ClO₄)₂·6H₂O favors the formation of crystal **2** in the presence of 2-butanol, while the spontaneous resolution reaction of **1** with Cd(ClO₄)₂·6H₂O biases the formation of crystal **3** in the presence of ethanol.

Enantiomeric crystals *P*-**2** and *M*-**3** can also be obtained as desired by changing the solvent with preformed *P*-**2** or *M*-**3**. In the absence of an organic solvent [or hydrothermal (water as solvent) reaction conditions], the chirality of the homochiral crystals obtained can sometimes be *P* (positive split Cotton effect) or sometimes be *M* (negative split Cotton effect), which results in a rough statistical distribution of 1:1. This is also true when the same glass vessel (test tube or flask) and the same mother liquid are used for repeated crystallization. This would suggest that the chirality is essentially governed by chance, that is, by the chirality that happens to the first-separating nucleus serving as the seed for subsequent crystal growth and not by that of any external chiral sources such as impurities.

Crystals of **2** adopt enantiomorphous pairs space group (*P*6₁22 and *P*6₅22) with a Flack value suggesting that the absolute configuration of **2** should be *P*6₁22.⁹ The local coordination geometry around the Cd center can be best described as a slightly distorted octahedron composed of four N coordinating atoms that form an equatorial plane with two O coordinating atoms of perchlorate ion occupying apical positions (Fig. 2). It is worth noting that only one of the four O atoms of the perchlorate ion is involved in coordination to the Cd center, and ligand **1** acts as bidentate spacer that connects two Cd atoms together through the two N atoms of two pyridyl rings of **1**. Furthermore, from

Figure 2 it is interesting to see that whole crystal only contains homochiral ligand (*R,R*)-**1**, without (*S,S*)-**1**. This suggests that a spontaneous resolution process took place in this case. The crystal should be homochiral not heterochiral as shown in Scheme 3. This consequently results in the formation of a 1D infinite homochiral chain, as shown in Figure 2b. Consecutive cadmium centers in the chain are bridged by ligand pairs with the same handedness. Inspection of Figure 2a, which shows the structure of **2**, reveals the presence of a void between consecutive cadmium centers. In the space-filling diagram this region indicated by blue shading and its size, and taking van der Waals radii into account, it suggests that a small guest molecule may be unable to neatly fit into this chiral pocket (Fig. 2b). Finally the bond distances of Cd–N and Cd–O are normal while the bond lengths of C–C, and C–N are unexceptional.

At first glance the 1-D coordination polymer appears to be unremarkable but on closer inspection, the interaction of this chain with neighboring chains in the *c*-direction makes this a most fascinating crystal structure. Large spaces lie between consecutive naphthyl groups in the chain, which allow equivalent neighboring chains to slot neatly together, as shown in Figure 2c and d. Although not indicated in the figures for reasons of clarity, slots along one side of a single chain are occupied by an infinite number of parallel chains.¹⁰

By virtue of ligand chirality, the slots may be considered as chiral and it would appear that the meshing of the polymer chains in the slots is most favorable when the slots have the same chirality. A consequence of this is that all the chains have the same handedness in a single crystal. Although all chains are perpendicular to this unique axis, the meshing between chains causes neighboring chains stacked in the *c*-direction to be rotated by 60° relative to each other around the *c*-axis. Consecutive rotations of 60° in these chains result in a sixfold screw axis, as shown in Figure 3.

Complex **3**, which contains the (*S,S*)-enantiomer of ligand **1**, is isostructural to that of **2**, as depicted in Figure 4. It is therefore unsurprising to find crystals of **3** also adopting an enantiomorphous space group (*P*6₁22 and *P*6₅22) with a Flack value suggesting that the absolute configuration of **3** should be *P*6₅22. Also, from Figure 4 it is interesting to see that whole crystal only contains the homochiral ligand (*S,S*)-**1**, without (*R,R*)-**1**. This implies that the crystals of **2** and **3** are enantiomorphous pairs. As expected, the slots in **3** have the opposite handedness to those found in the crystals of **2** and have consecutive rotations of the chains in the opposite direction. A comparison of the difference in the stacking of the chains along the *c*-axis in both **2** and **3** is shown in Figure 3, which clearly depicts these complexes to be enantiomorphous pairs with a relationship similar to that in Man between right-handedness and left-handedness. Similarly, the bond distances of Cd–N and Cd–O are normal while the bond lengths of C–C, and C–N are unexceptional. Evidently, it is worth making a comparison with the bond distances of **2** to

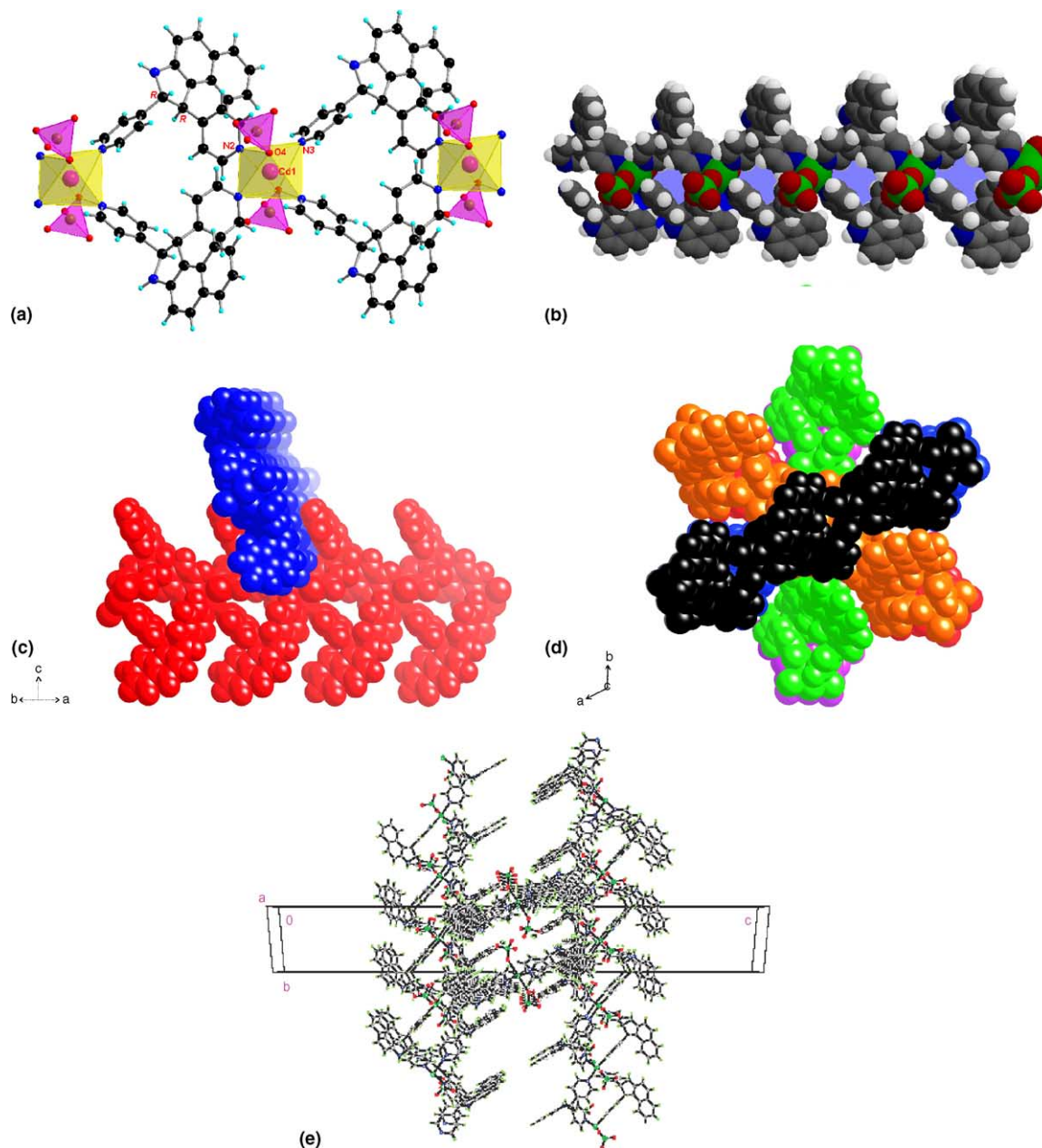
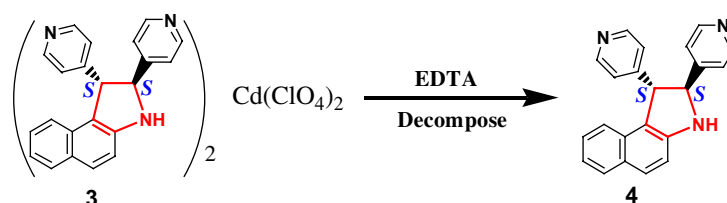
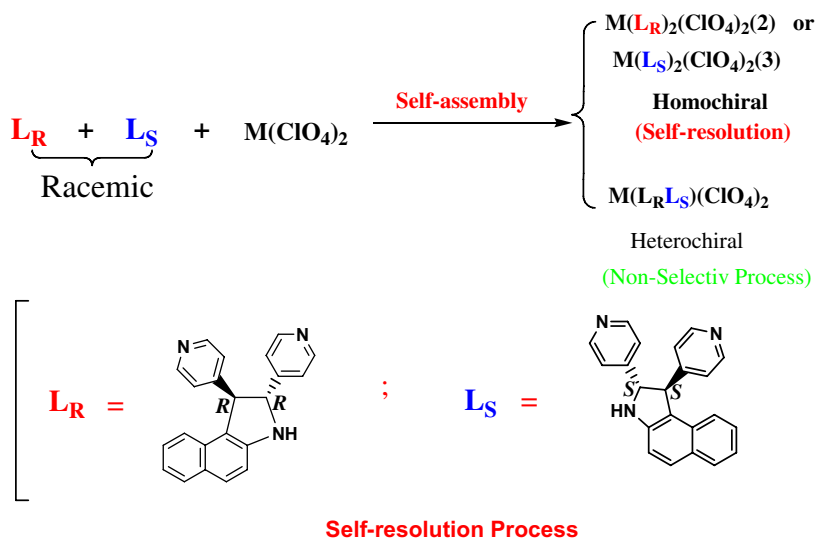


Figure 2. 1D coordination polymer of **2** in which the local coordination geometry around Cd center can be best described as a slightly octahedron, indicating the presence of *R,R*-1. Key bond distances (Å) and angles (°): Cd(1)–N(2)^{#1} 2.309(5), Cd(1)–N(2) 2.309(5), Cd(1)–N(3)^{#2} 2.328(5), Cd(1)–N(3)^{#3} 2.328(5), Cd(1)–O(4) 2.384(5), Cd(1)–O(4)^{#1} 2.384(5), N(3)–Cd(1)^{#4} 2.328(5); N(2)^{#1}–Cd(1)–N(2) 88.2(3), N(2)^{#1}–Cd(1)–N(3)^{#2} 92.68(19), N(2)–Cd(1)–N(3)^{#2} 169.08(19), N(2)^{#1}–Cd(1)–N(3)^{#3} 169.08(19), N(2)–Cd(1)–N(3)^{#3} 92.68(19), N(3)^{#2}–Cd(1)–N(3)^{#3} 88.5(3), N(2)^{#1}–Cd(1)–O(4) 102.99(19), N(2)–Cd(1)–O(4) 83.56(19), N(3)^{#2}–Cd(1)–O(4) 85.64(19), N(3)^{#3}–Cd(1)–O(4) 87.92(18), N(2)^{#1}–Cd(1)–O(4)^{#1} 83.56(19), N(2)–Cd(1)–O(4)^{#1} 102.99(19), N(3)^{#2}–Cd(1)–O(4)^{#1} 87.92(18), N(3)^{#3}–Cd(1)–O(4)^{#1} 85.64(19), O(4)–Cd(1)–O(4)^{#1} 171.0(3) [Symmetry transformations used to generate equivalent atoms: #1 $x - y, -y, -z$; #2 $x - y + 1, -y, -z$; #3 $x + 1, y, z$; #4 $x - 1, y, z$]. (b) The representation of a space-filling diagram of **2** in which the blue shading represents intra-chain voids. (c) A space-filling representation of part of the structure of **2** showing how neighboring chains slot together as they stack along the *c*-direction. (d) A space-filling representation of part of the structure of **2** viewed along the *c*-axis. Consecutive chains (each of different color) are rotated relative to each other by 60° about the *c*-axis. (e) A perspective packing view of **2** along the *a*-axis.



Scheme 2.



Scheme 3.

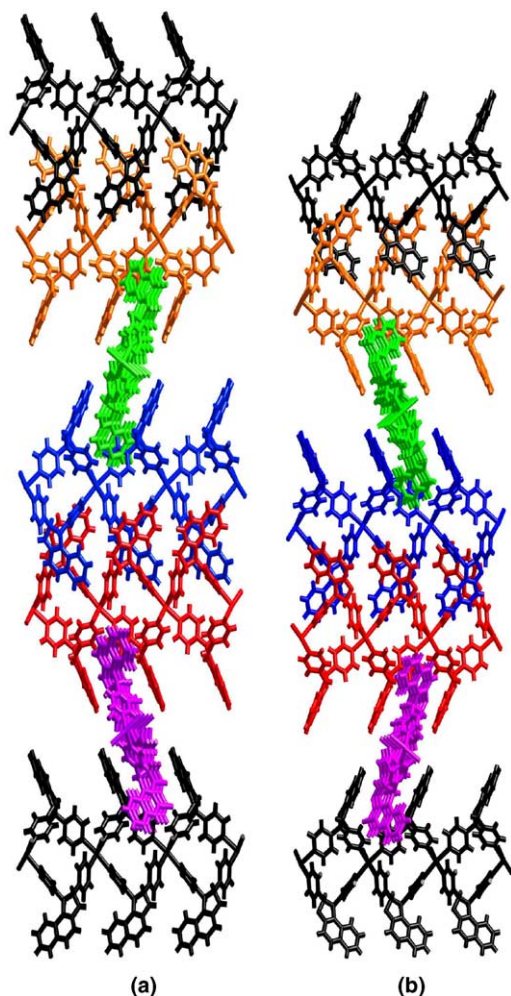


Figure 3. A stick representation showing how the chains stack together in the *c*-direction (vertical) in (a) **2** and (b) **3**.

those of **3**, finding that the bond lengths of Cd–N [2.309(5)–2.328(5) Å] and Cd–O [2.384(5) Å] in **2** are al-

most identical to those found in **3** [Cd–N for 2.314(5)–2.330(4) Å] and [Cd–O for 2.392(4) Å].

It is well documented in the literature that the crystal growth of NaClO_3 from pure aqueous solutions of the metal salt can proceed with high ee values with mechanical stirring. Herein, we found high ees can also be obtained for *P*- and *M*-crystals of **2** and **3** through the metal-coordinated spontaneous resolution in different solvents. While a 1:1 statistical distribution of *P*- and *M*-crystals were observed, this was comparable to that found in the mechanical stirring of NaClO_3 .^{5d,e} Despite this, we found that the reaction with 2-butanol as a solvent biased the formation of *P*-crystals of **2** while the analogous reaction with ethanol as solvent biased the formation of *M*-crystals of **3**. These experimental results demonstrate that the magnitude and direction of the bias can be selectively generated toward either the *P*- or *M*-forms by changing the solvent although the exact mechanism for this selectivity is currently unclear.

The spontaneous resolution achieved upon formation of a metal-coordination polymer prompted us to attempt separation of the homochiral crystals and furnish the ligand in its enantiomerically pure form. Crystals of **3** were mechanically separated into groups according to each crystal identical CD spectra in solid state. The KBr containing crystals of **3** are soluble in water, which permitted their extraction from an aqueous ethanol solution containing EDTA (Scheme 2). Recrystallization from a solution of EtOH containing organic ligand **1** furnished plate crystals with an approximate dimension of $0.20 \times 0.20 \times 0.14$ mm that were determined by X-ray single crystal analysis to be enantiomerically pure (*S,S*)-**1**, which crystallized in the chiral space group $P2_12_12_1$ as shown in Figure 5. The dihedral angles between the planes occupied by the indole ring and the pyridine rings are equal to 114° and 33° , respectively. This contrasts significantly to the same dihedral angles found in the structure of a racemic crystalline sample, which are equal to 96.9° and 98.8° , respectively.⁶ The

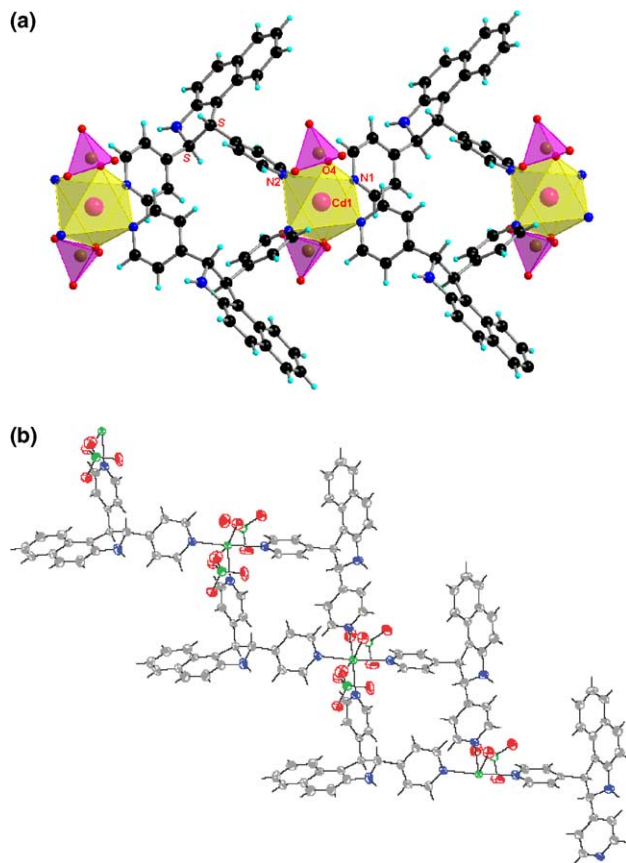


Figure 4. 1D coordination polymer of **3** in which the local coordination geometry around the Cd center can be best described as slightly octahedron, indicating the presence of (*S,S*)-**1**. Key bond distances (Å) and angles (°): Cd(1)–N(2) 2.314(4), Cd(1)–N(2)^{#1} 2.314(4), Cd(1)–N(1)^{#2} 2.330(4), Cd(1)–N(1)^{#3} 2.330(4), N(1)–Cd(1)^{#4} 2.330(4), Cd(1)–O(4)^{#1} 2.392(4), Cd(1)–O(4) 2.392(4); N(2)–Cd(1)–N(2)^{#1} 88.4(2), N(2)–Cd(1)–N(1)^{#2} 92.59(15), N(2)^{#1}–Cd(1)–N(1)^{#2} 168.93(15), N(2)–Cd(1)–N(1)^{#3} 168.93(15), N(2)^{#1}–Cd(1)–N(1)^{#3} 92.59(15), N(1)^{#2}–Cd(1)–N(1)^{#3} 88.5(2), N(2)–Cd(1)–O(4)^{#1} 103.43(15), N(2)^{#1}–Cd(1)–O(4)^{#1} 83.47(16), N(1)^{#2}–Cd(1)–O(4)^{#1} 85.57(16), N(1)^{#3}–Cd(1)–O(4)^{#1} 87.64(15), N(2)–Cd(1)–O(4) 83.47(16), N(2)^{#1}–Cd(1)–O(4) 103.43(15), N(1)^{#2}–Cd(1)–O(4) 87.64(15), N(1)^{#3}–Cd(1)–O(4) 85.57(16), O(4)^{#1}–Cd(1)–O(4) 170.5(2). [Symmetry transformations used to generate equivalent atoms: #1 $x - y, -y, -z$; #2 $x + 1, y, z$; #3 $x - y + 1, -y, -z$; #4 $x - 1, y, z$]. (b) 1D chain representation of **3** drawn 30% ellipsoid probability along *a*-axis.

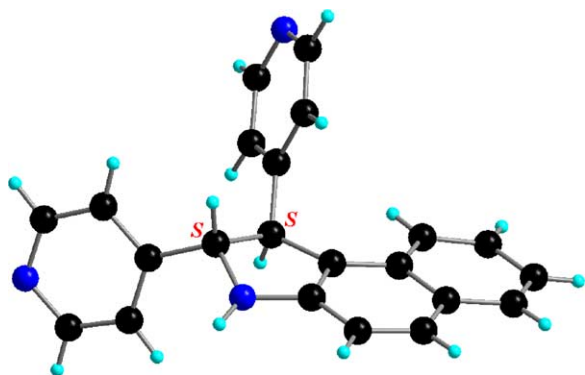


Figure 5. A perspective view of enantiomerically pure ligand **4**.

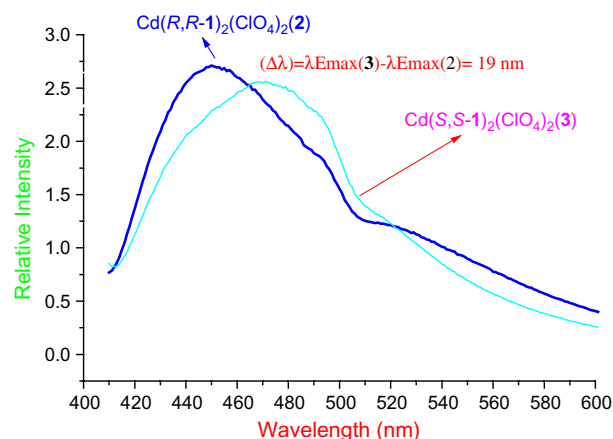


Figure 6. Fluorescent emission spectra of **2** and **3** in the solid state at room temperature.

bond distances of C–C and C–N are comparable to those found in **2** and **3**, and also are unexceptional.

At this point, it is interesting to note that the solid state fluorescent emission measurements of **2** and **3** in the powdered state show a moderate difference in maximum emission peaks ($\Delta\lambda = 19$ nm) between the *P*- and *M*-enantiomorphous forms. As shown in Figure 6, a maximum emission peak at ca. 450 nm can be observed for **2**, while a maximum emission peak at ca. 469 nm is found for **3**. This suggests that complexes **2** and **3** can be discriminated by fluorescence spectroscopy and should hold promising prospects in the development of new chiral fluorescent sensing devices.

3. Conclusion

In summary, we have demonstrated that *P*- and *M*-enantiomorphous pair crystals *P*-(**2**) and *M*-(**3**) can be obtained from the self-resolution of a one-pot reaction of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with **1** under different solvothermal conditions. The isolation and structural characterization of these enantiomorphous pair crystals by X-ray crystallography is unprecedented. The results herein provide strong encouragement that crystal engineering can be used to develop helpful methodologies for the separation of racemic mixtures to give enantiomerically pure products that may have technological applications, through spontaneous resolution, a process that involves noncovalent interactions of metal complexes at the supramolecular level and solvent symmetry breaking transitions.

4. Experimental

4.1. Synthesis of **2**

A sample of 0.331 g (1 mmol) $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 0.323 g (2 mmol) **1** was ground and mixed thoroughly. The reagents were loaded into a thick-walled Pyrex tube

(~25 cm long). After addition of 1 mL water and 2 mL 2-butanol, the tube was frozen with liquid N₂, evacuated under vacuum and sealed with a flame, and then placed inside an oven at 110 °C for 4 days and gave *P*-Cd(*R,R*,-1)₂(ClO₄)₂ **2** in 25% yield based on **1**. IR (KBr, cm⁻¹): 3375(m), 1615(s), 1520(w), 1431(w), 1370(w), 1314(w), 1281(w), 1250(w), 1125(vs), 1038(s), 928(w), 824(m), 791(w), 752(w), 706(w), 627(m), 557(w).

4.2. Synthesis of **3**

Prepared following the same procedure as that for **2** except with ethanol to replace of 2-butanol. IR (KBr, cm⁻¹): 3375(m), 1615(s), 1521(w), 1431(w), 1371(w), 1315(w), 1281(w), 1249(w), 1123(vs), 1036(s), 927(w), 823(w), 791(w), 750(w), 706(w), 627(m), 555(w).

4.3. Synthesis of (*S,S*)-**1**

Carefully selected crystals of **3** were treated with EDTA in the solution of water and EtOH and refluxed for 4 h. The resulting solution was extracted with CHCl₃ and the solvent evaporated under reduced pressure and recrystallized from a solution of EtOH to give (*S,S*)-**1**. IR (KBr, cm⁻¹): 3298(m), 3029(w), 2869(w), 1624(m), 1594(s), 1521(m), 1407(m), 1365(m), 1275(m), 1253(m), 1211(m), 1050(w), 994(w), 947(w), 869(w), 820(s), 758(m), 699(m), 610(m), 566(w), 499(w).

4.4. Estimation of ee values

Forty pieces of pale yellow single crystals were randomly chosen. Each crystal (~5 mm long and ~0.1 mg in weight) was grounded with KBr and fabricated in the form of pellet. Crystals with resulting CD spectra exhibiting identical Cotton effect accounted for 32 of the 40 pieces of crystals obtained. The ee value was = (32 – 8)/40 = +0.6 for *P*-Cd(*R,R*,-1)₂(ClO₄)₂ **2**. Homochiral crystallization was confirmed by observing that all 32 pieces of the single crystals showed the same sign of CD of a similar intensity. Similarly, The ee value = (12 – 28)/40 = –0.4 for *M*-Cd(*S,S*,-1)₂(ClO₄)₂ **3**.

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- Crystal data for **2**: C₄₄H₃₄Cl₂N₆O₈Cd, *M* = 958.07, hexagonal, *P*6₁22, *a* = 10.5488(5), *c* = 68.256(4) Å, *α* = *γ* = 90°, *β* = 120°, *V* = 6577.8(6) Å³, *Z* = 6, *D*_c = 1.451 mg m⁻³, *R*₁ = 0.0498, *wR*₂ = 0.1124, *μ* = 0.679 mm⁻¹, *S* = 0.623, Flack *χ* = –0.02(6). For space group *P*6₅22, *R*₁ = 0.0670, *wR*₂ = 0.1602, *S* = 0.725 with a Flack value of 1.03(7); Crystal data for **3**, C₄₄H₃₄Cl₂N₆O₈Cd,

$M = 958.07$, hexagonal, $P6_522$, $a = 10.5446(3)$, $c = 68.265(3)$ Å, $V = 6573.3(4)$ Å³, $Z = 6$, $D_c = 1.452$ mg m⁻³, $R_1 = 0.0444$, $wR_2 = 0.1002$, $\mu = 0.679$ mm⁻¹, $S = 0.558$, Flack $\chi = 0.01(5)$. For space group $P6_122$, $R_1 = 0.0501$, $wR_2 = 0.1178$, $S = 0.599$ with a Flack value of 1.00(5). The low Flack parameter indicates that the absolute configurations of **2** and **3** are correct; Crystal data for (S,S)-**1**, C₂₂H₁₇N₂, $M = 323.39$, orthorhombic, $P2_12_12_1$, $a = 9.2598(7)$, $b = 9.4617(8)$, $c = 19.1452(16)$ Å, $V = 1677.4(2)$ Å³, $Z = 4$, $D_c = 1.281$ mg m⁻³, $R_1 = 0.0417$, $wR_2 = 0.1191$, $T = 293$ K, $\mu = 0.077$ mm⁻¹, $S = 0.862$. The structures were solved with Direct methods using the program SHELXTL.¹¹ All nonhydrogen atoms were located from the trial structure and refined anisotropically with SHELXTL using the full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. Crystallographic data (excluding structure factors) for the complexes have been deposited with the Cambridge Crystallographic Data

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