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Synthesis and ferroelectric properties of platinum(II) complexes with chiral isoxazoline ligand



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Xiao-Peng Zhang, Jian Liu, Jing-Xuan Zhang, Jia-Hao Huang, Cheng-Zhang Wan, Cheng-Hui Li*, Xiao-Zeng You*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

Four chiral square-planar (SP-4) alkynylplatinum(II) complexes Pt(L)(C = C-Ph) (1), Pt(L)(C = C-Ph-Br)(2), $Pt(L)(C = C-Ph-CH_3)$ (3) and $Pt(L)(C = C-Ph-OCH_3)$ (4) (L = (15,5S)-6,6-dimethyl-3'-(pyridin-2-yl)-4'H-spiro[bicyclo[3.1.1]heptane-2,5'-isoxazole]) were prepared by the complexation of ligand L with K₂PtCl₄ and subsequent treatment with corresponding alkynes. Their structures were characterized by single crystal X-ray diffraction and electronic circular dichroism (CD) spectra. Although there are little differences in the molecular structures, these complexes exhibit significantly different molecular packing modes in their crystal structures. Moreover, complexes 1 and 4 crystallize in the polar space group P_{21} , while complexes 2 and 3 crystallize in the nonpolar space groups (I222 for 2 and $P_{21}_{21}_{21}$ for 3, respectively). Consequently, complexes 1 and 4 show distinct ferroelectric behaviors and nonlinear optical properties. To the best of our knowledge, our study represents the first example of chiral platinum(II) complexes demonstrating ferroelectric properties.

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1. Introduction

Ferroelectric materials, which possess a spontaneous electric polarization that can be reversed by the application of an external electric field, are of great interest due to their versatile applications in the field of electronics and optics, such as ferroelectric random access memory (FeRAM) [1,2], ferroelectric field-effect transistor (FeFET) [3,4] and anomalous ferroelectric photovoltaics [5–7]. According to the definition, the ferroelectric materials must possess a permanent dipole moment and this moment must be reversible in the presence of an applied voltage. A prerequisite for ferroelectric materials is that they crystallize in a space group belonging to one of the ten polar point groups (C_1 , C_s , C_2 , C_3 , C_3 , C_3 , C_4 , C_4 , C_6 , C_6 , V). The origins of ferroelectricity include displacive motion, order–disorder transformation and indirect type [8].

Molecular-based ferroelectric materials bear some advantages as compared to the typical inorganic ABO₃-type ferroelectrics. For example, molecule-based complexes have larger spontaneous polarization because of polar groups in the organic ligands. Neutral mononuclear molecule-based ferroelectric materials can be evaporated at lower temperature than ionic inorganic compounds by chemical vapor deposition (CVD) methods, making the fabrication of ferroelectric devices more convenient and controllable. Moreover, the ferroelectric properties of molecular crystals can be easily tailored by chemical modification. A large number of ferroelectric molecular crystals have been reported in recent years [9–13]. Particularly, introduction of chiral groups has shown to be effective to create molecular polar crystal with ferroelectric properties [14–17].

Platinum(II) complexes are always inclined to adopt squareplanar geometry, many of which show prominent conductivity and intriguing spectroscopic properties as a result of Pt-Pt and π - π stacking interaction [18–24]. By incorporation of specifically tailored ligands (such as bulky or chiral ligands), the planarity of platinum(II) complexes could be reasonably distorted, which produces the corresponding molecular chirality [25-29]. In the literature, numerous of chiral platinum(II) complexes have been reported and their application in asymmetric catalysis and medicinal chemistry have been described [30-33]. However, no reports have been devoted to their ferroelectric properties. In this work, we obtained four square-planar platinum(II) complexes containing chiral bidentate isoxazoline ligand: Pt(L)(C = C-Ph)(1), Pt(L)(C = C-Ph)(1)Ph-Br) (2), $Pt(L)(C \equiv C-Ph-CH_3)$ (3) and $Pt(L)(C \equiv C-Ph-OCH_3)$ (4) (L = (15,5S)-6,6-dimethyl-3'-(pyridin-2-yl)-4'H-spiro[bicyclo[3.1.1])heptane-2,5'-isoxazole]) (Scheme 1). Their structures were determined via X-ray crystallgraphy data. The chirality of these complexes was determined by CD spectroscopy. Moreover, the ferroelectric and dielectric properties of complexes 1 and 4 also have been studied.



^{*} Corresponding authors. Tel.: +86 25 83592969; fax: +86 25 83314502. *E-mail addresses*: chli@nju.edu.cn (C.-H. Li), youxz@nju.edu.cn (X.-Z. You).

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Scheme 1. Synthesis of the L and complexes 1–4 (1, R = H; 2, R = Br; 3, R = CH₃; 4, R = OCH₃).

2. Experimental

2.1. Materials and methods

All reagents were purchased from commercial suppliers and used as received. Mass spectra were acquired on LCQ Fleet ESI Mass Spectrometer. ¹H NMR spectra were obtained using a DRX 500 NMR spectrometer. Chemical shifts are referenced to TMS. Coupling constants are given in hertzs. UV–Vis spectra were measured by UV-3600 spectrophotometer using a quartz cell of 1 cm length in dichloromethane solution. ECD spectra were recorded by a Jasco J-810 spectropolarimeter. Emission spectra were recorded by a Hitachi F-4600 luminescence spectrometer. The Electric hysteresis loops were recorded by a Ferroelectric Tester Precision Premier II by using powdered samples in pellets at room temperature. The temperature dependence of the dielectric constant and dielectric loss at $10^2 - 10^6$ Hz frequencies were measured by using a dielectric impedance analyzer, Concept 80 system (Novocontrol, Germany).

2.2. Synthesis of the ligand L and complexes 1-4

2.2.1. Synthesis of (E)-picolinaldehyde oxime

This compound was prepared following the literature method [34]. Hydroxylamine hydrochloride (11 mmol) were added in a solution of 2-pyridinecarboxaldehyde (1 mmol) in EtOH/H₂O (40 mL, 9:1) mixture under argon atmosphere. NaOH (1.1 mmol) in H₂O (2 mL) was then added slowly. The mixture was heated at 80 °C for overnight. The solvents were removed in vacuo and the residue was extracted with CH₂Cl₂. The organic phase was separated and dried (Na₂SO₄), and the solvent was evaporated. At last the product was purified by chromatography on a silica gel column using PE:EA = 1:1. Yield: 95%. ¹H NMR (500 MHz, CDCl₃): δ 10.96 [s, 1H], δ 8.65 [d, 1H, J = 5 Hz], δ 8.41 [s, 1H], δ 7.89 [d, 1H, J = 8 Hz], 7.74 [td, 1H, J = 8 Hz, 1.5 Hz], 7.30 [t, 1H, J = 6 Hz]. MS (ESI) (m/z): [M]⁺ Anal. Calc. for C₆H₆N₂O: 122.1. Found: 122.2.

2.2.2. Synthesis of the ligand L

This compound was prepared following the literature method [35,36]. A mixture of (E)-picolinaldehyde oxime (5 mmol) and N-chlorosuccinimide (NCS, 5 mmol) in anhydrous CHCl₃ (15 mL)

and pyridine (0.5 ml) was stirred at 60 °C for 30 min under argon atmosphere. After the completion of the chlorination reaction, a CHCl₃ solution of beta-pinene (5 mmol) and Et₃N (1 mL) was added slowly and stirred at 50 °C for 2 h. The solvent was evaporated in vacuo and the residue was extracted with CH₂Cl₂. The organic phase was separated and dried (Na₂SO₄), and the solvent was removed. At last the product was purified by chromatography on a silica gel column using PE:EA = 10:1. Yield: 80%. ¹H NMR (500 MHz, CDCl₃): δ 8.61 [d, 1H, *J* = 5 Hz], δ 8.03 [d, 1H, *J* = 7.5 Hz], δ 7.72 [td, 1H, *J* = 7.5 Hz, 2 Hz], δ 7.29 [t, 1H, *J* = 5 Hz], δ 3.35 [d, 2H, *J* = 3 Hz], δ 2.41–2.46 [m, 1H], δ 1.97–2.04 [m, 2H], δ 1.87–1.90 [m, 1H], δ 1.66 [d, 1H, *J* = 10.5 Hz], δ 1.28 [s, 3H], δ 1.02 [s, 3H]. MS (ESI) (*m*/*z*): [M]⁺ Anal. Calc. for C₁₆H₂₀N₂O: 256.2. Found: 256.5.

2.2.3. Synthesis of Pt(L)Cl₂

A HCl (0.2 M) solution of L (1 mmol) and K₂PtCl₄ (1 mmol) was stirred for 5 h at reflux under argon atmosphere. Yellow precipitates were obtained, which were filtrated and washed with water and *n*-hexane. Yield: 85%. ¹H NMR (500 MHz, DMSO): δ 9.26 [d, 1H, *J* = 5.5 Hz], δ 8.36 [t, 1H, *J* = 8 Hz], δ 7.97 [d, 1H, *J* = 8 Hz], δ 7.83 [t, 1H, *J* = 7.5 Hz], δ 3.40–3.43 [m, 2H], δ 2.30–3.33 [m, 2H], δ 2.27–2.29 [m, 2H], δ 1.95–2.00 [m, 2H], δ 1.80–1.83 [m, 1H], δ 1.42 [d, 1H, *J* = 9.5 Hz], δ 1.27 [s, 3H], δ 0.97 [s, 3H]. MS (ESI) (*m*/*z*): [M]⁺ Anal. Calc. for C₁₆H₂₀Cl₂N₂OPt: 521.1. Found: 521.3.

2.2.4. Synthesis of $Pt(L)(C \equiv C - Ph)(1)$

Complex **1** was synthesized as describe of the Sonogashira method [37]. In the absence of light, phenylacetylene (1.2 mmol) were added in a anhydrous dichloromethane solution of Pt(L)Cl₂ (1 mmol), Et₃N and CuI (10 mg) under argon atmosphere. After stirring at room temperature for 24 h, the solvent was evaporated in vacuo, and the product was purified by chromatography on a silica gel column using PE:EA = 1:1. Yield: 85%. ¹H NMR (500 MHz, CDCl₃): δ 9.26 [d, 1H, *J* = 5.5 Hz], δ 8.00 [t, 1H, *J* = 7.5 Hz], δ 7.65 [d, 1H, *J* = 7 Hz], δ 7.46 [d, 4H, *J* = 7.5 Hz], 7.42 [t, 1H, *J* = 6.5 Hz], 7.28 [t, 2H, *J* = 7.5 Hz], 7.23 [t, 2H, *J* = 7.5 Hz], 7.18 [t, 1H, *J* = 7.5 Hz], 7.12 [t, 1H, *J* = 7.5 Hz], δ 3.56 [d, 1H, *J* = 17 Hz], δ 3.19 [d, 1H, *J* = 17 Hz], δ 1.72–1.77 [m, 1H], δ 1.68 [d, 1H, *J* = 11 Hz],

 δ 1.60 [s, 1H], δ 1.25 [s, 3H], δ 0.86 [s, 3H]. MS (ESI) (*m*/*z*): [M]⁺ Anal. Calc. for C₃₂H₃₀N₂OPt: 653.2. Found: 653.4.

2.2.5. Synthesis of $Pt(L)(C \equiv C - Ph - Br)$ (2)

Compound **2** was obtained with the same procedure for **1**. Yield: 75%. ¹H NMR (500 MHz, CDCl₃): δ 9.40 [d, 1H, 5 Hz], δ 8.06 [t, 1H, *J* = 7.5 Hz], δ 7.58 [d, 1H, *J* = 7.5 Hz], δ 7.54 [t, 1H, *J* = 7 Hz], 7.40 [d, 2H, *J* = 8 Hz], 7.34 [q, 6H, *J* = 8.5 Hz], δ 3.35 [d, 1H, *J* = 17.5 Hz], δ 3.17 [d, 1H, *J* = 17.5 Hz], δ 2.65–2.72 [m, 1H], δ 2.34–2.41 [m, 2H], δ 2.17–2.22 [m, 1H], δ 2.05–2.08 [m, 2H], δ 1.84–1.86 [m, 1H], δ 1.68 [d, 1H, *J* = 10.5 Hz], δ 1.30 [s, 3H], δ 0.95 [s, 3H]. MS (ESI) (*m*/*z*): [M]⁺ Anal. Calc. for C₃₂H₂₈Br₂N₂OPt: 812.0. Found: 812.4.

2.2.6. Synthesis of $Pt(L)(C \equiv C - Ph - CH_3)$ (3)

Compound **3** was obtained with the same procedure for **1**. Yield: 79%. ¹H NMR (500 MHz, CDCl₃): δ 9.22 [s, 1H], δ 8.00 [t, 1H, *J* = 7.5 Hz], δ 7.68 [d, 1H, *J* = 8 Hz], δ 7.40 [t, 1H, *J* = 7.5 Hz], 7.36 [d, 4H, *J* = 7.5 Hz], 7.10 [d, 2H, *J* = 8 Hz], 7.05 [d, 2H, *J* = 7.5 Hz], δ 3.60 [d, 1H, *J* = 18 Hz], δ 3.19 [d, 1H, *J* = 17.5 Hz], δ 2.61–2.69 [m, 1H], δ 2.37 [s, 3H], δ 2.34 [s, 3H], δ 2.28–2.33 [m, 3H], δ 1.97–2.01 [m, 2H], δ 1.72–1.76 [m, 1H], δ 1.67 [d, 1H, *J* = 11 Hz], δ 1.63 [s, 1H], δ 1.25 [s, 3H], δ 0.86 [s, 3H]. MS (ESI) (*m*/*z*): [M]⁺ *Anal.* Calc. for C₃₄H₃₄N₂OPt: 681.2. Found: 681.4.

2.2.7. Synthesis of $Pt(L)(C \equiv C - Ph - OCH_3)$ (4)

Compound **4** was obtained with the same procedure for **1**. Yield: 66%. ¹H NMR (500 MHz, CDCl₃): δ 9.28 [d, 1H, *J* = 5 Hz], δ 8.01 [t, 1H, *J* = 7.5 Hz], δ 7.64 [d, 1H, *J* = 8 Hz], δ 7.41–7.42 [m, 1H], 7.39 [d, 4H, *J* = 7.5 Hz], 6.83[d, 2H, *J* = 9.5 Hz], 6.78 [d, 2H, *J* = 9.5 Hz], δ 3.82 [s, 3H], δ 3.80 [s, 3H], δ 3.54 [d, 1H, *J* = 18 Hz], δ 3.18 [d, 1H, *J* = 17 Hz], δ 2.62–2.69 [m, 1H], δ 2.28–2.37 [m, 3H], δ 1.97–2.02 [m, 2H], δ 1.74–1.78 [m, 1H], δ 1.67 [d, 1H, *J* = 11 Hz], δ 1.61 [s, 1H], δ 1.24 [s, 3H], δ 0.87 [s, 3H]. MS (ESI) (*m*/*z*): [M]⁺ *Anal.* Calc. for C₃₄H₃₄N₂O₃Pt: 713.2. Found: 713.3.

Table 1	l
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Crystallographic data of complexes 1-4.

2.3. X-ray structure determination

Single-crystal X-ray diffraction measurements were carried out with a Bruker SMART APEX CCD diffractometer operating at room temperature. Intensities were collected with graphite monochromatized Mo K α radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA, using $\omega/2\theta$ scan mode. The data reduction was performed with the Bruker SAINT package [38]. Absorption corrections were performed using the sadabs program [39]. The structures were solved by direct methods and refined on F^2 by full-matrix leastsquares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms in all two structures. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as riding mode, with C-H = 0.93 Å (methane) or 0.96 Å (methyl) and $U_{iso}(H) = 1.2 U_{eq} (C_{methane})$ or $U_{iso}(H) = 1.5 U_{eq}$ (C_{methyl}). The water hydrogen atoms were located in the difference Fourier maps and refined with an O-H distance restraint [0.85(1) Å] and $U_{iso}(H) = 1.5 U_{eq}(O)$. All computations were carried out using the SHELXTL-97 program package [40].

3. Results and discussion

3.1. Crystal structures description

Complexes **1–4** were firstly obtained as orange powders from reactions between $Pt(L)Cl_2$ and corresponding alkynes. All single crystals suitable for X-ray diffraction analysis were obtained by recrystallization in CH_2Cl_2 /acetone. Complexes **1** and **4** crystallize in the polar space group ($P2_1$) of a monoclinic system, while complexes **2** and **3** crystallize in *1*222 and $P2_12_12_1$ of orthorhombic system, respectively (Table 1). As shown in the Fig. 1, the asymmetrical unit of complex **1** contains one molecule of Pt(L)(C=C-Ph). The Pt–C bond lengths vary from 1.906(14) to 1.963(10) Å, whereas the Pt–N distances lie between 2.032(7) and 2.107(11) Å. All these bond lengths are in the typical range [41,42]. Both of the phenylacetylene rings are displaced towards

	1	2 0.5C ₃ H ₆ O	3 C ₃ H ₆ O	4 0.5CH ₂ Cl ₂
Formula	C ₃₂ H ₃₀ N ₂ OPt	$C_{67}H_{62}Br_4N_4O_3Pt_2$	C ₃₇ H ₄₀ N ₂ O ₂ Pt	C ₆₉ H ₇₀ Cl ₂ N ₄ O ₆ Pt ₂
Mr	653.67	1681.03	739.80	1512.37
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	P21	1222	$P2_{1}2_{1}2_{1}$	P21
a (Å)	6.1674(4)	11.6252(17)	6.977(2)	11.209(2)
b (Å)	13.0314(8)	16.326(3)	13.006(4)	16.942(4)
c (Å)	16.6433(11)	35.041(5)	35.853(11)	16.362(4)
α (°)	90.00	90.00	90.00	90.00
β(°)	91.2790(10)	90.00	90.00	92.010(3)
γ(°)	90.00	90.00	90.00	90.00
V (Å ³)	1337.29(15)	6650.7(17)	3253.2(17)	3105.3(11)
Z	2	4	4	2
T (K)	296(2)	296(2)	296(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
$D_{\text{calc}} \left(\text{g/cm}^{-3} \right)$	1.623	1.679	1.510	1.617
μ (mm ⁻¹)	5.273	6.651	4.347	4.642
F(000)	644	3248	1480	1500
θ (°)	1.98-25.00	1.38 -25.00	1.93 -25.00	2.17-26.00
Reflections measured	6809	13343	15665	17029
Unique reflections	4462	5836	5716	10983
R _{int}	0.0389	0.0662	0.0505	0.0411
Reflections with $F^2 > 2\sigma(F^2)$	3796	4844	5531	9165
Number of parameters	325	365	385	756
Goodness-of-fit (GOF) on F^2	1.024	1.076	1.083	1.079
$R_1^{a}, w R_2^{b} [I > 2\sigma(I)]$	0.0403, 0.0865	0.0637, 0.1675	0.0448, 0.1074	0.0415, 0.0679
R_1, wR_2 (all data)	0.0469, 0.0881	0.0760, 0.1735	0.0464, 0.1080	0.0495, 0.0694
$\Delta ho_{ m max,} \Delta ho_{ m min}$ (e Å ⁻³)	2.560, -1.013	2.956, -2.855	2.598, -2.359	2.595, -1.135

^a $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|.$

^b $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}.$



Fig. 1. The <code>ortep</code> view of complex 1 with 30% probability level ellipsoids. H atoms are omitted for clarity.

the same side of the coordination plane which is similar to the observation by Zelewsky and co-workers [43]. The molecule of **1** deviates from planar configuration slightly (the torsion angle between isoxazoline plane and phenylacetylene rings is 164.09° and 158.14°). The molecular structures of **2–4** are very similar to that of **1** (Figs. S1–S3). As shown in Table 2, the variance in bond distances and bond angles in **1–4** are insignificant, indicating that the electron donating/withdrawing effect of the substituents in the phenylacetylene ligands are not strong enough to alter the structural parameters.

The molecules of **1–4** are arranged into one-dimensional chains along *a* axis via two different modes (head-to-head mode or staggered fashion). In complexes **1** and **3**, the molecules adopt a head-to-head packing mode (Figs. 2 and S4). Distinct $C-H\cdots\pi$

Table 2

Structural parameters determined by X-ray single crystal diffraction.

	1	2	3	4
Bond length				
Pt1-C1	1.918(10)	1.906(14)	1.944(9)	1.912(10)
Pt1-C2	1.954(11)	1.953(14)	1.947(9)	1.963(10)
Pt1-N1	2.076(8)	2.107(11)	2.088(7)	2.063(8)
Pt1-N2	2.032(7)	2.041(11)	2.040(8)	2.062(8)
Pt2-C3				1.908(10)
Pt2-C4				1.927(10)
Pt2-N3				2.032(8)
Pt2-N4				2.055(8)
Bond angles				
C1-Pt1-N1	96.0(3)	98.3(5)	94.1(3)	94.3(4)
C1-Pt1-N2	173.4(3)	175.6(5)	171.5(3)	171.8(4)
C1-Pt1-C2	87.7(4)	88.7(6)	92.1(3)	86.5(4)
N1-Pt1-N2	77.3(3)	77.4(5)	77.7(3)	77.5(3)
N1-Pt1-C2	176.0(4)	172.8(5)	171.9(4)	178.9(4)
N2-Pt1-C2	98.9(4)	95.6(5)	96.3(3)	101.7(4)
C3-Pt2-N3				171.0(4)
C3-Pt2-N4				93.2(3)
C3-Pt2-C4				88.0(4)
N3-Pt2-N4				78.1(3)
N3-Pt2-C4				100.7(4)
N4-Pt2-C4				177.9(4)

and/or π - π interactions are observed within the one-dimensional chain. The shortest intermolecular Pt-Pt distances in complexes **1** and **3** are 7.797 and 8.054 Å, indicating the absence of metal-metal interaction, which is due to the large steric hindrance of chiral pinene groups when packing in the head-to-head mode. However, the molecules of **2** and **4** form dimers in a staggered fashion through Pt-Pt and π - π interactions. The dimers are then connected by solvent molecules in the crystal lattice via C-H··· π interaction to form one-dimensional chains (Figs. 3 and S5). The Pt-Pt interactions are quite weak in **2** and **4** with the Pt-Pt distances being 3.473 and 3.491 Å, respectively.

The one-dimensional chains are then aligned parallel to each other to form the three dimensional structure. There is also significant difference in the arrangement of molecules in *bc* plane. For **1** and **4**, the molecules are aligned in a zigzag fashion along *b* axis. The adjacent zigzag chains point to the same direction (Figs. 4 and S6). However, the direction of adjacent zigzag chains in complexes **2** and **3** are opposite to each other (Figs. 5 and S7). As each molecule has an intrinsic dipole moment, while the dipole moments are cumulative along the zigzag chain, the crystals of **1** and **4** are expected to derive a net dipole moment along the *b* axis. However, for complexes **2** and **3**, the net dipole moments within the zigzag chains will be cancelled by those of the adjacent zigzag chains, leading to the loss of polarity in the crystals. These structural features are consistent with the measurement of ferroelectric and non-linear properties (see below).

3.2. UV-Vis absorption and circular dichroism (CD) spectra

Fig. S8 shows the UV–Vis spectra of ligand L and complexes **1–4** in dichloromethane solution. The spectroscopic features are quite similar to their analogous complexes. The intense bands of complexes **1–4** at about 240–320 nm with ε exceeding 10⁴ L mol⁻¹ cm⁻¹ are originated from intraligand ${}^{1}\pi$ – π * (1 L) transitions involving ligand L and arylacetylide. In addition, the broad and weak lower energy bands ($\varepsilon > 10^{3}$ L mol⁻¹ cm⁻¹) near 400 nm are assigned as a 1 MLCT [5d(Pt) \rightarrow π *(diimine)] transition. A correlation between absorption energy and arylacetylide substitutents is observed and tabulated in the Table 3. It is evident that the 1 MLCT absorption shifts to lower energy (from 405 nm for **2** to 416 nm for **4**) as the donicity of arylacetylide increase (Br < H < CH₃ < OCH₃), which is consistent with the feature of MLCT transition.

The chirality of complexes **1–4** was confirmed by circular dichroism (CD) spectra (Fig. S8). The CD spectrum of the ligand L only shows positive Cotton effect at 262 nm. The dissymmetry of complexes **1–4** mainly comes from the intrinsic chirality of the ligand L, and all of them show positive Cotton effect at ca. 300 nm, with one extremely weak positive Cotton effects band at 410 nm.

3.3. Luminescent properties

As presented in the Fig. S9, all complexes are emissive in fluid solution at room temperature. The origin of emission band is contributed from triplet MLCT $[5d(Pt) \rightarrow \pi^*(diimine)]$ excited state [44,45]. The emission band shifts to lower energy as the electron-donating ability of the arylacetylide ligands increases (Table 3). The emission spectra of **1** and **2** exhibit vibrational progressional spacings (ca. 1300 cm^{-1}) which is the skeletal vibrational frequency of the ligand L. The profile of excitation spectra is similar to absorption spectra, which demonstrate efficient intersystem crossing of electronic excited state. The large stocks shifts also confirm that the emission originate from triplet excited states.

The solid-state emission spectra of all platinum(II) complexes are highly resolved (Fig. 6), and the emission energies in solid state are identical to that recorded in dichloromethane solution. Therefore, the emission in solid-state can be similarly identified as MLCT



Fig. 2. The one-dimensional chain structure of **1** along *a* axis, with dashed lines indicating the C-H \cdots π and π - π interactions. The H-atoms not involved in C-H \cdots π interactions are omitted for charity.



Fig. 3. The one-dimensional chain structure of **2** along *a* axis, with dashed lines indicating the Pt–Pt, C–H··· π and π – π interactions. The H-atoms not involved in C–H··· π interactions are omitted for charity.



Fig. 4. The molecular packing diagram of complex 1 in *bc* plane.

 $[5d(Pt) \rightarrow \pi^*(diimine)]$ excited state [46]. Although two packing modes are adopted and different Pt–Pt distances are exhibited, the energy of emissive state remained unchanged, suggesting that

the Pt–Pt interactions ($d_{Pt-Pt} > 3.4$ Å) in **2** and **4** are not strong enough to form MMLCT state upon excitation as in bis(σ -fluorophenylacetylide) platinum(II) complexes [47].



Fig. 5. The molecular packing diagram of complex 3 in bc plane.

Table 3Photophysical data in solution at 298 K.

Complex	$\lambda_{abs} (nm) (\varepsilon [L mol^{-1} cm^{-1}])$	$\lambda_{\rm em} ({\rm nm})$	$\Phi_{ m em}$
1	273 (29380), 408 (7920)	604	0.068
2	283 (30100), 405 (6920)	599	0.046
3	274 (28700), 411 (7000)	617	0.060
4	275 (32780), 416 (6940)	636	0.019

3.4. Ferroelectric and dielectric behaviors

The space group $P2_1$ of complexes **1** and **4** belong to point group C_2 , which is one of ten polar point groups, meeting for the prerequisite of ferroelectricity. Therefore, the ferroelectric properties of **1** and **4** were investigated at 298 K with compressed powder samples as shown in Figs. 7 and 8.





The ferroelectric measurements revealed that complex **1** indeed displays an obvious ferroelectric behavior and almost reaches the saturated polarization status with a remnant polarization (P_r) of ca. 0.08 μ C cm⁻² and E_c of ca. 4.7 kV cm⁻¹ by applying an electric field of 7 kV cm⁻¹ at 10 Hz. The saturation spontaneous polarization (P_s) is about 0.15 μ C cm⁻², which is compared with the typical ferroelectrics NaKC₄H₄O₆·4H₂O (Rosal salt; $P_s = 0.25 \ \mu$ C cm⁻²).

The ferroelectricity of complex **1** can be ascribed to the structural distortion like non-hydrogen ferroelectrics $BaTiO_3$ and $LiN-bO_3$ [48–51]. The complex adopts four-coordinated mode and deviates from planar configuration, resulting that the positive and negative charge centers separation to create a local dipole moment.

Complex **4** also crystallizes in the space group $P2_1$ and potentially has ferroelectric property. Ferroelectric study of powdered pellet sample clearly exhibits that an electric hysteresis loop was observed with a spontaneous polarization (*Ps*) of 0.12 μ C cm⁻²



Fig. 7. Ferroelectric hysteresis loop for complex 1 at 298 K.



Fig. 8. Ferroelectric hysteresis loop for complex 4 at 298 K.

and remnant polarization (Pr) of ca. 0.06 μ C cm⁻² when the electric field of 10 kV cm⁻¹ was applied.

In contrast, complexes **2** and **3** did not show ferroelectric effect, in accordance with their non-polar crystal structures.

The ferroelectricity is commonly confirmed by the existence of Curie point or dielectric anomaly. Therefore, we measured the temperature dependence of dielectric constants of **1** and **4**. As the melting point of complex **1** is about 438 K, the permittivity was recorded from 273 to 412 K. The ε' and ε'' remains almost unchanged in the range of 273–383 K for complex **1**, but a significant increase is observed at 398 K (Fig. 9 and Fig. 10). The ε' and ε'' did not show peak maximum up to 412 K. Therefore, the ferroelectric phase transition point, if it is in presence, would be higher than the melting point. The peak maximum was also not found in the dielectric loss.

The similar phenomena were also exhibited for complex **4** that the ε' and ε'' just have a raise upon increasing temperature, and no dielectric anomalies were observed (Figs. S10 and S11).

3.5. Second-order NLO properties

Both complexes **1** and **4** show distinct second-order NLO properties, while complexes **2** and **3** only exhibit very small NLO effects and can be neglected. By using the Kurtz powder method [52], the second harmonic generation (SHG) responses of complexes **1** and **4** are estimated to be 0.6 and 0.3 times that of urea, respectively.



Fig. 9. Temperature dependence of the dielectric constant ε' (real part) of **1** at various frequencies (1–10⁶ Hz).



Fig. 10. Temperature dependence of the dielectric constant ε'' (imaginary part) of **1** at various frequencies (1 10⁶ Hz).

According to our former study, the polarity of the crystal plays a key role in determining the physical properties [53]. As complex **3** crystallizes in the non-polar space group $P2_12_12_1$, their net dipole moments are cancelled by three perpendicular twofold screw axes, which lead to a smaller NLO effect. Complex **2** is similar to complex **3**, and its molecular polarity is neutralized by three perpendicular twofold axes.

However, both complexes **1** and **4** crystallize in the polar space group P_{2_1} , and they have only one twofold screw axes along the *b* direction, where the net dipole moments are expected. So it is reasonable that the larger second harmonic generation (SHG) responses of them are observed.

4. Conclusions

In this work, we report the synthesis and characterization of four platinum(II) complexes with chiral isoxazoline ligand. Although there are little differences in the auxiliary ligands, these complexes display two different packing arrangements and crystallize in three different space groups. The absorption and emission properties are more susceptible to the substitution groups in the auxiliary ligands rather than the molecular packing modes. However, the different crystal structures result in significant difference in crystal polarity. Complexes 1 and 4 crystallize in the polar space group *P*2₁, and consequently show distinct ferroelectric behaviors and nonlinear optical properties. Complexes 2 and 3 crystallize in the nonpolar space groups (I222 for **2** and $P2_12_12_1$ for **3**, respectively) and therefore no ferroelectric effect was observed. To the best of our knowledge, our study represents the first example of chiral platinum(II) complexes demonstrating ferroelectric properties.

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Appendix A. Supplementary data

CCDC 921963–921966 contain the supplementary crystallographic data for complexes **1–4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.poly.2013.05.024.

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