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Piezochroniic Luninescence	Promising phosphor
$f = \begin{pmatrix} H & H \\ H & H \\ H & H \\ H & H \\ Heating \end{pmatrix}$ $f = \begin{pmatrix} H & H \\ H & $	intramolecular m-stacking
Reversible piezochromism Chain length-dependent emission	Excellent redox reversibility Reduction in the degradation reaction

A series of iridium(III)-based phosphorescent dyes showing naked-eye visible and reversible piezochromic luminescent behavior are successfully synthesized. Moreover, they are promising luminescent materials with high quantum yields of 55~65%, excellent redox reversibility and relative stability.

Highlights

- Synthesis of Ir(III)-based dyes with different *N*-alkyl chains is described.
- ► They show naked-eye visible and reversible piezochromism.
- ► The chain length-dependent emissions are presented and investigated.
- ► The dyes exhibit high quantum yields, redox reversibility and good stability.
- ► The experimental results are rationalized by the theoretical calculations.

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Influence of alkyl chain lengths on the properties of iridium(III)-based piezochromic luminescent dyes with triazole-pyridine type ancillary ligands

Guo-Gang Shan, Hai-Bin Li, Hong-Tao Cao, Hai-Zhu Sun, Dong-Xia Zhu, Zhong-Min Su*¹

Institute of Functional Material Chemistry, Faculty of chemistry, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China.

^{*}To whom correspondence should be addressed. E-mail: <u>zmsu@nenu.edu.cn</u>

Fax: +86-431-85684009, Tel.: +86-431-85099108

Abstract

To investigate the relationship between structures and piezochromic luminescence behavior and to develop excellent materials for efficient light-emitting electrochemical cells, a series of iridium(III) complexes with different length of alkyl chains have been designed and synthesized. The results show that all complexes exhibit not only naked-eye visible and reversible piezochromic behavior, but chain length-dependent emission properties: the shorter the alkyl chain is, the more remarkable mechanochromic behavior and higher recrystallization temperature will be. In light of powder X-ray diffractometry and differential scanning calorimetric data, the interconversion between crystalline and amorphous states upon external stimuli is response for the present piezochromism. Additionally, these complexes show high quantum yields of $55 \sim 65\%$ in neat films as well as excellent redox reversibility. Despite changed alkyl chains are introduced into these complexes, the negligible effect on emitting colors and excited-state characters of them in both solutions and neat films have been observed. Such photophysical properties are also interpreted with the help of theoretical calculations. Moreover, the theoretical results suggest that the intrinsic intramolecular π - π stacking confirmed by the crystal structures can effectively restrict the opening of the structures in metal-centered excited-state, demonstrating their stability. The structure-property relationships and the results demonstrated here will help researchers develope and design more promising iridium(III)-based piezochromic materials and attractive phosphors for optical devices.

Keywords

Iridium(III) complex; Piezochromic luminescence; Chain length-dependent emission;

High quantum efficiency; Density functional theory

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1. Introduction

Organic luminophores that exhibit clear and vivid luminescence in the solid states have attracted tremendous attention due to their great potential in various photofunctional applications [1, 2]. The photophysical properties of these solid-state organic luminophores, for example emission color, strongly depend on the mode of molecular stacking and the intermolecular interactions [3, 4]. Accordingly, dynamic tuning and switching of solid-state luminescence can be achieved by means of the external stimulus that triggers the alteration of molecular arrangement motif [5-7]. Recently, the organic luminophores undergo a significant pressure-induced change in the emission color, termed piezochromic luminescent (PCL) materials, are growing rapidly [8-18]. Such materials exhibit reversible and obvious color change upon external mechanical forces but without chemical reactions, making them highly attractive alternative for both fundamental research and practical application. To this date, PCL behaviors for a few materials have been observed, including organic and inorganic complexes, liquid crystal materials, and polymer-based assemblies [19-27]. However, the number of such materials is still rare, especially for metal-contained complexes. To develop excellent PCL materials and establish clear structure-property relationship, the in-depth understanding of PCL phenomena at molecular level are essential. Thereby, it remains a great challenge to design new PCL materials and investigate the relationship between molecular packing and piezochromic behavior.

Organometallic iridium(III) complexes exhibiting high phosphorescence efficiency and rich photophysical properties as well as superior optical stability, have

emerged as promising candidates for high-tech applications such as organic light-emitting diodes (OLED), light-emitting electrochemical cells (LECs), chemical sensor, and biological probes, etc [28-32]. Recently, our group and others have developed a series of cationic iridium(III) complexes showing an interesting piezochromic behavior, and found that their emission color switch is generally attributed to a crystalline–amorphous phase transformation [33-36]. Based on this mechanistic proposal, the PCL behavior can be ingeniously switched by simply adjusting the substitution on ancillary ligands of the iridium(III) complexes [37]. In addition, iridium(III) complexes can provide a better structural control on excited-state properties and the optical output in different medias. Very recently, the multifunctional iridium(III) complexes simultaneously exhibiting aggregation-induced emission (AIE) and PCL properties have been realized by attaching the dendritic group into complexes or modifying ancillary ligand with carbazole unit [37, 38]. Despite these advances in iridium(III)-based PCL material, such materials are still in their infancy and more clear structure-property relationship has not been well addressed. Recent works on organic fluorescent PCL materials demonstrates that different long alkyl chains grafted on the materials not only can construct a series of new PCL materials with comparable molecular structure, but also provide an efficient way to study the relationship between the structure and PCL behavior [39-41]. Whereas, such great successes obtained through the flexible strategy in organic fluorescent PCL materials are still limited for metal complexes.

On the other hand, to realize efficient and long-lifetime light-emitting

electrochemical cells (LECs), cationic iridium(III) complexes with fascinating characteristics, such as high quantum efficiency especially in the neat film, excellent stability and redox reversibility, are highly desired [42-45]. And the exploitation of novel cationic iridium(III) complexes for the efficient and stable LECs is also rising significant interest in recent years [46-50]. If the different length of alkyl chains are attached to the ligands to construct a series of comparable molecular PCL cationic iridium(III) complexes that can meet the above-mentioned requirement for efficient LECs, which may be a "one stone two bird" design strategy. Keeping this in mind, we herein designed and prepared a new cationic iridium(III) complex $[(dfppz)_2(L1)]PF_6$ (complex 1) as shown in Scheme 1 and its analogues 2, 3, 4, and 5 with different length of alkyls. Their photophysical properties in the solid-states as well as solution have been investigated systematically. The results indicate that all complexes exhibit naked-eye visible PCL behavior with a color change from sky-blue to blue-green emitting and alkyl chain length dependent PCL properties. The emission color can be easily switched by grinding and heating. Comprehensive density functional theory (DFT) approach has been performed to gain insights into their photophysical properties in solutions as well as to evaluate the stability accommodated by intramolecular π - π stacking. The theoretical results suggest that the intrinsic intramolecular π -stacking in the complexes can effectively restrict opening of the structure in the ³MC state, indicative of their good stability. Combining with the high quantum efficiency in neat film and excellent redox reversibility, it is anticipated that these complexes are also attractive candidates for LECs.

Insert Scheme 1.

Scheme 1. Synthetic procedure and the chemical structures of complexes 1–5.

2. Experimental section

2.1. Materials and measurements

All reagents and solvents employed were commercially available and used as received without further purification. The solvents for syntheses were freshly distilled over appropriate drying reagents. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. ¹H NMR spectra were measured on Bruker Avance 500 MHz with tetramethylsilane as the internal standard. The molecular weights of ligands and complexes were tested by using electrospray-ionization mass spectroscopy and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry, respectively. UV-vis absorption spectra were recorded on Hitachi U3030 spectrometer. The emission spectra were recorded using the F-4600 FL spectrophotometer. The excited-state lifetime were measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photon counting technique. The photoluminescence quantum yields (PLQYs) of the neat film were measured in an integrating sphere. Cyclic voltammetry was performed on a BAS 100 W instrument with a scan rate of 100 mV s⁻¹ in CH₃CN solutions with the three-electrode

configuration: a glassy-carbon electrode as the working electrode, an aqueous saturated calomel electrode as the pseudo-reference electrode, and a platinum wire as the counter electrode, respectively. A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in CH₃CN was used as the supporting electrolyte, and the ferrocene/ferrocinium (Fc^+/Fc) potential was measured and selected as the internal standard.

2.2. Synthesis

2.2.1. Synthesis of ancillary the liangds

2-(1-methyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Metaz)

A mixture of 2-(3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine prepared according to previous report [51] (1.1 g, 5.0 mmol) and NaH (0.46 g, 20 mmol) in dry DMF (15 mL) was stirred at 0 °C for 10 min. Iodomethane (1.1 g, 7.5 mmol) in 5 mL DMF was added dropwise to the reaction mixture, and then the solution was stirred at room temperature for an additional 12 h. After that, the mixture was poured into the ice water, and extracted with CH₂Cl₂. The organic layer was washed with sodium bicarbonate solution and water for several times. Then, the organic layer was dried over anhydrous MgSO₄, filtered and then concentrated. The residue was purified by column chromatography (silica, ethyl acetate/petroleum ether = 1: 2) to yield a white powder **Metaz** (yield: 66%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.70 (d, *J* = 4.5 Hz, 1H), 8.33 (d, *J* = 8 Hz, 1H), 8.15–8.17 (m, 2H), 7.84–7.87 (m, 1H), 7.35–7.48 (m, 4H), 4.42 (s, 3H).

2-(3-phenyl-1-propyl-1*H*-1,2,4-triazol-5-yl)pyridine (Protaz)

The precursor 2-(3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (1.1 g, 5.0 mmol) was dissolved in acetone, and the equivalent KOH was added and the mixture was stirred for 0.5 h. Then, 1-bromopropane (0.73 g, 6.0 mmol) was added into the reaction mixture and the mixture was heated to reflux for overnight. After cooling to room temperature, the mixture was quenched by water and then extracted by dichloromethane. The organic layer was dried with Na₂SO₄ and the solvent was removed. The obtained residues was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:2) as the eluent to yield a light-yellow oil (60%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.62–8.63 (m, 1H), 8.30 (d, *J* = 8 Hz, 1H), 8.18–8.20 (m, 2H), 7.75–7.78 (m, 1H), 7.43–7.46 (m, 2H), 7.38–7.39 (m, 1H), 7.24–7.27 (m, 1H), 4.82 (t, *J* = 7.5 Hz, 1H), 1.95–1.99 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).

2-(1-pentyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Pentaz)

The synthetic procedure was similar to that of **Protaz** except that 1-bromopropane was used instead of 1-bromopentane. ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.66–8.67 (m, 1H), 8.31 (d, *J* = 8 Hz, 1H), 8.17–8.18 (m, 2H), 7.81–7.84 (m, 1H), 7.41–7.46 (m, 2H), 7.37–7.40 (m, 1H), 7.31–7.34 (m, 1H), 4.85 (t, *J* = 8 Hz, 2H), 1.92–1.98 (m, 2H), 1.33–1.37 (m, 4H), 0.88–0.89 (m, 3H).

2-(1-heptyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Heptaz)

¹H NMR (500 MHz, CDCl₃, ppm): δ 8.67–8.68 (m, 1H), 8.30–8.32 (m, 1H), 8.16–8.18 (m, 2H), 7.82–7.85 (m, 1H), 7.43–7.46 (m, 2H), 7.39–7.41 (m, 1H),

7.32–7.35 (m, 1H), 4.85 (t, *J* = 7 Hz, 2H), 1.92–1.96 (m, 2H), 1.23–1.37 (m, 8H), 0.87 (t, *J* = 7 Hz, 3H).

2-(1-nonyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Nontaz)

¹H NMR (500 MHz, CDCl₃, ppm): δ 8.66–8.68 (m, 1H), 8.30–8.31 (m, 1H), 8.16–8.18 (m, 2H), 7.82–7.85 (m, 1H), 7.43–7.47 (m, 2H), 7.37–7.41 (m, 1H), 7.32–7.35 (m, 1H), 4.85 (t, *J* = 7.5 Hz, 2H), 1.93–1.96 (m, 2H), 1.24–1.37 (m, 12H), 0.87 (t, *J* = 6 Hz, 3H).

2.2.2. Synthesis of the chloro-bridged dimer [Ir(dfppz)₂Cl]₂

The organometallated dimer $[Ir(dfppz)_2Cl]_2$ was synthesized from reaction of $IrCl_3 \cdot 3H_2O$ (0.81 g, 2.32 mmol) with 1-(2,4-difluorophenyl)-1*H*-pyrazole (dfppz, 0.92 g, 5.10 mmol) in 2-ethoxyethanol and water mixture (V:V = 3:1, 40 mL) for 24 h. The mixture was treated with water (30 mL) to induce precipitation of the off-white solid. The product was filtered out and washed with diethyl ether followed by ethanol, and dried (yield: 79%).

2.2.3 Synthesis of the complexes

Synthesis and characterization of complex 1

A solution of ligand **Metaz** (0.50 g, 2.1 mmol) and the dichloro-bridged diiridium complex $[Ir(dfppz)_2Cl]_2$ (1.2 g, 1.0 mmol) in 1,2-ethandiol (30 mL) was heated at 150 °C for 15 h in the dark. After cooling to room temperature, the 20 mL methanol solution was added into the mixture. Then, the aqueous solution of NH₄PF₆ (2.0 g in 100 mL of deionized water) was slowly added into the reaction mixture under stirring. The obtained suspension was filtrated, and washed with water and methanol. The

crude product was purified by silica gel column chromatography using dichloromethane/ethyl acetate (6:1) and the resulting powders were recrysatallized from dichloromethane and petroleum ether mixture to give complex **1** as a light-green solid, m.p. 347 °C (yield 81%). ¹H NMR (500 MHz, d₆–DMSO, ppm): δ 8.64 (d, *J* = 8.5 Hz, 2H), 8.51 (d, *J* = 2.5 Hz, 1H), 8.38 (t, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 5.5 Hz, 1H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.74 (t, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.05–7.10 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 2.5 Hz, 1H), 6.80 (t, *J* = 2.5 Hz, 1H), 6.66–6.67 (m, 1H), 5.56 (dd, *J_I* = 8.0 Hz, *J*₂ = 2.0 Hz, 1H), 5.06 (dd, *J_I* = 8.0 Hz, *J*₂ = 2.0 Hz, 1H), 4.51 (s, 3H). ¹⁹F NMR (470 MHz, d₆-DMSO, ppm): -66.57 (d, *J* = 710.64 Hz, 6F), -109.54 (dd, *J_I* = 8.46 Hz, *J*₂ = 14.57 Hz, 1F), -111.23 (dd, *J_I* = 5.17 Hz, *J*₂ = 11.75 Hz, 1F). MS (MALDI-TOF): m/z 787.1 (M–PF6). The related complexes (**2**, **3**, **4** and **5**) were prepared using the similar procedures.

Synthesis and characterization of complex 2

Light-green solid; m.p. 281 °C (Yield 78%). ¹H NMR (500 MHz, d₆–DMSO, ppm): δ 8.62–8.64 (m, 2H), 8.49 (d, J = 2.5 Hz, 1H), 8.38 (t, J = 8.0 Hz, 1H), 8.01 (d, J = 5.5 Hz, 1H), 7.86 (d, J = 2.0 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 2.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.05–7.13 (m, 3H), 7.02 (d, J = 7.5 Hz, 2H), 6.85 (t, J = 2.5 Hz, 1H), 6.78 (t, J = 2.5 Hz, 1H), 6.62–6.67 (m, 1H), 5.57 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.5$ Hz, 1H), 5.07 (dd, $J_1 = 8.0$ Hz, $J_1 = 2.0$ Hz, 1H), 4.74–4.89 (m, 2H), 2.01–2.06 (m, 2H), 1.02 (t, J = 7.5 Hz, 3H). ¹⁹F NMR (470 MHz, d₆-DMSO, ppm): -66.57 (d, J = 2.5 Hz, 1H)

710.64 Hz, 6F), -109.57 (dd, $J_1 = 7.89$ Hz, $J_2 = 14.10$ Hz, 1F), -111.24 (dd, $J_1 = 5.17$ Hz, $J_2 = 8.93$ Hz, 1F), -119.81 (dd, $J_1 = 6.11$ Hz, $J_2 = 12.22$ Hz, 1F), -121.72 (dd, $J_1 = 5.64$ Hz, $J_2 = 12.22$ Hz, 1F). MS (MALDI-TOF): m/z 815.2 (M–PF6).

Synthesis and characterization of complex 3

Light-green solid; m.p. 293 °C (Yield 80%). ¹H NMR (500 MHz, d₆–DMSO, ppm): δ 8.60–8.64 (m, 2H), 8.49 (d, J = 2.5 Hz, 1H), 8.39 (t, J = 8.0 Hz, 1H), 8.01 (d, J = 5.5 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.74 (t, J = 6.5 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.05–7.13 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 2.5 Hz, 1H), 6.77 (t, J = 2.5 Hz, 1H), 6.62–6.67 (m, 1H), 5.57 (dd, $J_I = 8.0$ Hz, $J_2 = 2.5$ Hz, 1H), 5.07 (dd, $J_I = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H), 4.77–4.90 (m, 2H), 2.00–2.01 (m, 2H), 1.33–1.37 (m, 4H),0.89 (t, J = 7.5 Hz, 3H). ¹⁹F NMR (470 MHz, d₆-DMSO, ppm): -66.57 (d, J = 710.64 Hz, 6F), -109.58 (dd, $J_I = 8.46$ Hz, $J_2 = 14.57$ Hz, 1F), -111.23 (dd, $J_I = 5.64$ Hz, $J_2 = 8.46$ Hz, 1F), -119.80 (dd, $J_I = 4.70$ Hz, $J_2 = 12.22$ Hz, 1F), -121.71 (dd, $J_I = 5.17$ Hz, $J_2 = 12.22$ Hz, 1F). MS (MALDI-TOF): m/z 843.2 (M–PF6).

Synthesis and characterization of complex 4

Light-green solid; m.p. 285 °C (Yield 72%). ¹H NMR (500 MHz, d₆–DMSO, ppm): δ 8.60–8.64 (m, 2H), 8.49 (d, J = 2.5 Hz, 1H), 8.39 (t, J = 8.0 Hz, 1H), 8.01 (d, J = 5.5 Hz, 1H), 7.86 (d, J = 2.0 Hz, 1H), 7.74 (t, J = 6.5 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.05–7.13 (m, 3H), 7.02 (d, J = 7.5 Hz, 2H), 6.86 (t, J = 2.5 Hz, 1H), 6.77 (t, J = 2.5 Hz, 1H), 6.62–6.66 (m, 1H), 5.57 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.5$ Hz, 1H), 5.08 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H), 4.75–4.91 (m, 2H), 1.99–2.03 (m,

2H), 1.25–1.40 (m, 8H), 0.86 (t, J = 7.0 Hz, 3H). ¹⁹F NMR (470 MHz, d₆-DMSO, ppm): -66.57 (d, J = 711.11 Hz, 6F), -109.57 (dd, $J_I = 6.11$ Hz, $J_2 = 8.46$ Hz, 1F), -111.23 (dd, $J_I = 6.11$ Hz, $J_2 = 8.46$ Hz, 1F), -119.81 (dd, $J_I = 4.70$ Hz, $J_2 = 12.22$ Hz, 1F), -121.72 (dd, $J_I = 4.70$ Hz, $J_2 = 12.22$ Hz, 1F). MS (MALDI-TOF): m/z 871.3 (M–PF6).

Synthesis and characterization of complex 5

Light-green solid; m.p. 246 °C (Yield 62%). ¹H NMR (500 MHz, d₆–DMSO, ppm): δ 8.60–8.64 (m, 2H), 8.49 (d, J = 2.0 Hz, 1H), 8.36–8.39 (m, 1H), 8.01 (d, J = 4.5 Hz, 1H), 7.85 (d, J = 2.0 Hz, 1H), 7.74 (t, J = 6.5 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.05–7.14 (m, 3H), 7.02 (d, J = 7.0 Hz, 2H), 6.85 (t, J = 2.5 Hz, 1H), 6.76 (t, J = 2.5 Hz, 1H), 6.63–6.67 (m, 1H), 5.56 (dd, $J_I = 8.0$ Hz, $J_2 = 1.5$ Hz, 1H), 5.08 (dd, $J_I = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H), 4.76–4.90 (m, 2H), 1.98–2.01 (m, 2H), 1.23–1.40 (m, 12H), 0.82–0.85 (m, 3H). ¹⁹F NMR (470 MHz, d₆-DMSO, ppm): -66.57 (d, J = 711.11 Hz, 6F), -109.57 (dd, $J_I = 9.40$ Hz, $J_2 = 14.10$ Hz, 1F), -111.22 (dd, $J_I = 0.94$ Hz, $J_2 = 14.10$ Hz, 1F), -119.82 (dd, $J_I = 5.17$ Hz, $J_2 = 11.28$ Hz, 1F), -121.74 (dd, $J_I = 4.70$ Hz, $J_2 = 9.40$ Hz, 1F). MS (MALDI-TOF): m/z 899.3 (M–PF6).

2.2.4. Theoretical calculations

Calculations on the ground and excited electronic state of complexes were investigated by performing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP level [52]. The 6-31G* basis sets were employed for optimizing the C, H, N atoms and the LANL2DZ basis sets for Ir atom.

An effective core potential (ECP) replaces the inner core electrons of iridium leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir(III). The geometry of the metal-centered triplet (³MC) were fully optimized and was calcluated at the spin-unrestricted UB3LYP level with a spin multiplicity of 3. All expectation values calculated for S² were smaller than 2.05. All calculations reported here were carried out with the Gaussian 09 software package [53].

2.2.5. X-ray crystallography study

Data collection of complexes **1** and **2** were performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo K_a radiation ($\lambda = 0.71069$ Å) at 293 K. Absorption corrections were performed by using the multi-scan technique. The crystal structure was solved by Direct Methods of SHELXTL-97 [54] and refined by full-matrix least-squares techniques using SHELXTL-97 within WINGX. The hydrogen atoms of aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. Anisotropic thermal parameters were used to refine all non-hydrogen atoms except for part of nitrogen and carbon atoms. The detailed crystallographic data and structure refinement parameters are summarized in Table S1 (see supporting information). Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 951185 (1) and 951186 (2) contain the supplementary crystallographic data for this paper.

3. Results and discussion

3.1. Synthesis and Crystal Structure

The ligands ancillary easily reaction of were prepared by the 2-(3-phenyl-1H-1,2,4-triazol-5-yl) pyridine with corresponding halohydrocarbon in the presence of the strong base condition. Simple heating of the mixture of the dimeric iridium(III) intermediates and the ancillary ligands in 1,2-ethandiol and subsequent the counter-ion exchange reaction produced the target complexes with high yields (70% ~ 81%). All complexes were fully characterized by ¹H NMR and ¹⁹F NMR spectrometry as well as MADIL-TOF. In addition, the molecular structures of complexes 1 and 2 were further determined by X-ray crystallography. Both complexes reveal the distorted octahedral geometry around the Ir atom with two cyclometalated ligands and one ancillary ligand, as shown in Fig. 1. The two cyclometalated ligands both adopt a mutually eclipsed configuration with two nitrogen atoms residing at trans locations. It is noted that the bond lengths Ir-Nancillary ligand are significantly longer than those of N_{cyclometalated ligand}, as a result of the strong *trans* influence of the carbon donors. For example, in the case of complex 1, the Ir-N bond lengths in the ancillary ligand Ir1-N5 and Ir1-N6 are 2.167(11) Å and 2.158(10) Å, respectively, which are longer than those in cyclometalated ligand Ir1–N2 1.985(12) Å and Ir1–N4 2.017(11) Å (see Table S2). These observations have also been made in complex 2 and the related cationic Ir(III) complexes [55, 56]. In addition, the robust π - π intramolecular interactions between the phenyl ring of the corrsponding ancillary ligands and phenyl ring of one of cyclometalated ligands are observed in complex 1

and **2**, with a centroid-centroid distance of 3.864 and 3.685 Å, respectively (Fig. 1). The inherent intramolecular π - π stacking in such cationic iridium(III) complexes can suppress the opening of the structure in metal-center (³MC) excited-state effectively, leading to reduction of the degradation reaction to some extent when they are used as emitting materials in LECs, and hence the efficient and stable devices [57-59].

Insert Fig. 1.

Fig. 1. Crystal structures of complexes 1 (a) and 2 (b). Thermal ellipsoids are drawn at 30% probability. The PF_6 counter-anion and hydrogen atoms are omitted for clarity.

3.2. Photophysical properties in the solid-state and pizochromic behavior

The emission spectra of all as-synthesized solid powders are measured (see Fig. 2 and Fig. S1) and the numerical data are summarized in Table 1. All complexes exhibit strong sky-blue emission with peak wavelength of 461–472 nm, as shown in the inset of Fig. 2. When these solid state powders obtained through column chromatography (namely, as-synthesized powders) were ground in a ceramic mortar, naked-eye visible luminescent color change could be clearly observed. Herein, we take complex **1** as an example. For clearly, the as-synthesized samples and ground samples were hereafter abbreviated as the letters "**a**" and "**g**", respectively (e.g., the sample **1a** is the as-synthesized complex **1** through column chromatography; **1g** is the ground sample of **1a**). Upon grinding, the emission color change of sample **1a** is depicted in Fig. 2a,

showing a significant emission red-shift from sky-blue ($\lambda_{em} = 466$ nm) to blue-green $(\lambda_{em} = 483 \text{ nm})$. The similar phenomenon can be observed for other samples 2a–5a. It is noted that the grinding-induced spectral shifts ($\Delta \lambda_{PCL} = \lambda_{ground} - \lambda_{as-synthesized}$) of samples **1a–5a** are alkyl length-dependent, although they all exhibit obvious piezochormic luminescence behavior. As shown in Fig. 2, 5a shows much smaller the grinding-induced spectral shift of 8 nm compared with that of **1a** ($\Delta \lambda_{PCL} = 17$ nm). The $\Delta \lambda_{PCL}$ for 2a, 3a and 4a are 20, 21, 10 nm, respectively. In other words, the sample 5a with a longest alkyl chain among these samples exhibits the smallest emission red shift. The result also suggests that alkyl chains play a functional role in turning the PCL behavior and the order of color changes induced by grinding is similar to the previously reported fluorescent PCL materials. It is known the PCL materials are potential candidates for optical recording application. To primarily test the optical recording potential for them, the solid state sample 5a was then outspread on a filter paper and the word "Dye" was written on the filter paper using a spatula. The blue-green "Dye" can be observed clearly on the blue "paper" with the naked eye under the UV light (Fig. S2).

Insert Fig. 2.

Fig. 2. Emission spectra of complexes **1** and **5** in the solid states. The letters "a" and "g" represent as-synthesized and ground samples, respectively.

Insert Table 1.

 Table 1
 Solid-state photophysical data and DSC results of complexes 1–5 in various states.

Interestingly, the emission color of ground samples can easily be reverted to the sky-blue emitting samples upon heating at about 220 °C for 5 min. The corresponding emission spectra of the heated sample, **1h–5h**, are revealed in Figs. S3 and S4. Further grinding the sky-blue emitting heated samples can result in blue-green emitting powders again. The color changes in solid state can repeat many times, suggesting that these samples also possess an excellent reversibility in the switching processes. In addition, the emission profile of the heated samples with relatively long alkyl chain, such as **3h**, **4h** and **5h** exactly match those of the original unground states compared with **1h** and **2h** (see Figs. S3 and S4). The ¹H NMR and MALDI-TOF spectra of them in various solid state have been also measured. Almost no changes were found for these spectra in different states, indicating that the emission color changes of them might be caused by physical processes during the grinding and heating process [60, 61].

Moreover, the photoluminescence decays of the complexes in the solid powders before and after grinding have been also investigated and the excited-state lifetimes for the different samples in various states are listed in Table 1. It can be seen that, for all complexes, the weighted mean lifetimes $\langle \tau \rangle$ of as-synthesized samples **1a–5a** and their ground samples are significantly different, respectively. However, in the case of cationic iridium(III) complex without PCL behavior, the lifetimes of as-synthesized

and ground sample have almost the same $\langle \tau \rangle$ values. These results suggest that the PCL materials based on iridium(III) complexes show significantly different time-resolved emission-decay between the as-synthesized and ground samples. Thus, the changes in emission color in association with $\langle \tau \rangle$ values of PCL samples **1a–5a** should be caused by altering the mode of solid-state molecular packing and/or the intermolecular interactions after grinding.

Insert Fig. 3.

Fig. 3. PXRD patterns of as-synthesized samples 1a and 2a and ground samples 1g and 2g.

3.3. Powder X-ray diffraction and differential scanning calorimetry of solid samples

A possible mechanism was previously proposed to explain PCL behavior of transition metal-based complexes, that is, efficient grinding results in the amorphous powders instead of original crystalline structures (as-synthesized samples). To gain an insight into the present PCL behavior of theses iridium(III) complexes, the powder X-ray diffraction (PXRD) experiment was performed on both the as-synthesized and ground samples. As shown in Fig. 3, the measured PXRD peaks of as-synthesized samples, **1a** and **2a**, are consistent with their single-crystal diffraction data, showing sharp and intense reflections. Such intense reflection peaks are also observed for other samples

3a–5a. The results indicate that the as-synthesized samples should be well-ordered aggregates, i.e. crystalline structure. In contrast, the diffractograms of the ground samples exhibit weak and broad PXRD pattern, suggesting that the amorphous states formed instead of the original ordered structures. The existence of a small amount crystalline feature in PXRD curves of ground samples is possibly caused by incomplete grinding. In addition to PXRD investigations, the differential scanning calorimetry (DSC) study was carried out to further confirm the formation of the amorphous powders upon grinding. No endo- and/or exothermic peaks are detected before the isotropic metal transition of the as-synthesized samples, except for 1a that shows higher melt point than 300 °C, as shown in Fig. 4a. However, for ground samples, each DSC curves firstly appears an exothermic recrystallization peak, and then endothermic melting peaks are detected, which are similar to the melting points of corresponding crystalline state samples. It is known that the amorphous solid will become less viscous and the molecules may obtain enough freedom of motion to spontaneously arrange themselves into crystalline forms upon heating. Thus, the results suggest that the amorphous ground samples investigated here are all metastable states. If the ground samples are heated above their recrystallization temperatures, they will restore to thermodynamically stable crystals through the exothermic recrystallization process. Noticeably, 5g with long alkyl chains exhibits lower recrystallization temperatures compared with those of 1g-4g, which may attribute to the much weaker intermolecular interactions in 5g than others. The results show that the recrystallization temperatures for ground samples are also chain

length-dependent; that is the longer the alkyl chains, the lower recrystallization temperatures, as revealed in Fig. 4b. These findings are similar to recently reported PCL materials based on organic small molecules [41].

Insert Fig. 4.

Fig. 4. DSC curves of as-synthesized samples (a) and ground samples (b).

Photophysical properties in the soultion and film

The obtained complexes 1-5 were easily solvent in common organic solvent, such as CH₂Cl₂, THF and CH₃CN. The UV-vis absorption and emission spectra recorded for all cationic iridium(III) complexes 1-5 in CH₃CN solution at room temperature (RT) are presented in Fig. 5a and the numerical results are tabled in Table 2. They exhibit almost indential absorption spectra in same solutions. The intense absorption bands below 300 nm can be assigned to the ligand-centered ${}^{1}\pi-\pi^{*}$ transition, and the low-energy absorption bands that occur in the region longer than 300 nm are ascribed to the 1 MLCT, 3 MLCT (metal-to-ligand charge transfer) and ${}^{3}\pi-\pi^{*}$ transition. Upon photoexcitation, all the investigated complexes exhibit bright green emission in CH₃CN solutions with the peaks at about 505 nm. The significant variations of emission intensity and excited-state lifetime observed between degassed and aerated CH₃CN solution and microsecond time scale lifetime highlight their phosphorescent nature. It is noted that their emission profiles are amlost indentical despite the different alkyl chains attached on the acllicary ligands, showing broad and

featureless emission spectra. Generally, for cationic iridium(III) complexes, three excited states contribute to the observation of light emission, namely, ³MLCT, ³LLCT and LC ${}^{3}\pi$ - π^{*} , The emission spectra from ${}^{3}MLCT$ and ${}^{3}LLCT$ states are usually broad and featureless, while the obvious structured emission band are always attributed to the LC ${}^{3}\pi$ - π * one. Thus, the emissive excited states of them take on much more ³MLCT and ³LLCT character than LC ${}^{3}\pi$ - π *, which is further confirmed by the low-temperature emission and TD-DFT calculations (vide infra). Upon cooling the CH₃CN solution to 77 K, the emission spectra of them are obviously blue-shifted compared with those at RT but are still borad and featureless [42, 49]. These emission properties at 77 K further suggest that the emissions of them mainly originate from ³MLCT mixed with some content of ³LLCT states. To gain insight into the nature of the emissive excited state involved in the emission process of all complexes, the quantum chemical calculations employing DFT were performed (see experimental section). The low-lying triplet states of them are calculated based on their optimized ground geometry through TD-DFT. The corresponding excitation energies and molecular orbitals involved in the excitations are summarized in Tables S3 and S4. On the basis of the TD-DFT calculation, the T_1 states of all complexes originate from the excitation of HOMO \rightarrow LUMO with different contribution (see Table S4). As shown in Tables S3, the HOMOs of them mainly reside on the cyclometalated ligands and d orbital of iridium atom, while the LUMOs locates on the ancillary ligands. Accordingly, the observed emission bands of all complexes should mainly originate ³MLCT (Ir→ancillary ligands) ³LLCT from (cyclometalated the and

ligands—ancillary ligands) states, which is compliance with our experimental data. Moreover, the alkyl chains on the ancillary ligand have no contributed to the HOMO and LUMO orbitals, rationally explaining that the alkyl chains have little influence on emission spectra. The PL spectra in neat film are also recorded at RT and the corresponding emission spectra are placed in the Fig. S6. It is observed that the neat film emission spectra are also board and show a common red-shift with respect to those in CH₃CN solutions, which may caused by the molecular aggregation and triplet–triplet interaction when going from solutions to neat film. These complexes exhibit considerable quantum efficiency of 54.9% ~ 65.3%, indicating that they would be excellent emitting materials used in the optical devices.

Insert Fig. 5.

Fig. 5. Absorption and emission spectra of complexes 1-5 in CH₃CN solution with concentration of 1×10^{-5} M at room temperature (a) and 77 K (b).

Insert Table 2.

 Table 2. Photophysical and electrochemical properties of complexes 1–5.

3.4. Electrochemical properties

The electrochemical behaviors of complexes **1–5** have been determined by cyclic voltammertry (CV) and the redox potentials are listed in Table 2. According to the previous reports, the reduction of cationic iridium(III) complexes usually occurs on

the ancillary ligands [45, 49]. In addition, all complexes process almost identical emission energy as mentioned above. Thus, it can be proposed that these complexes exhibit similar oxidation and reduction processes in CV curves. As expected, the electrochemical data show that each complex exhibits a reversible redox processes in CH₃CN solution with oxidation peaks at ~ +1.23 V and reduction peaks at ~ -1.81 V versus Fc/Fc⁺, respectively (see Fig. S7). The different alkyl chains play a functional role in their PCL behavior but have neglectable influence on the photophysical properties of them and even the electrochemical behaviors. Moreover, these complexes showing redox reversibility indicates that both the holes (upon oxidation) and electrons (upon reduction) can be easily transported when employing them as emission materials, which is beneficial for the application in LECs [30, 57].

Insert Fig. 6.

Fig. 6. The minimum-energy structure calculated for the ³MC state of complex 1.

3.5. Metal-centered states (³MC)

Cationic iridium(III) complex as an active component layer in LECs offer several advantages over conventional OLEDs such as simple device structure, low turn-on voltage as well as independence of the work function. Recently, a great deal of effort has been invested into optimization of LECs inculding emission color, luminescent quantum and trun-on time, etc. Although these advances in iridium(III)-based LECs, the relatively short lifetime of the devices that mainly originates from the degradation

process of the complexes in metal-centered (³MC) states [57], has been observed. Essentially, ³MC state is defined as the excitation of an electron from the occupied $t_{2g}(d\pi)$ HOMO to the unoccupied $e_{2g}(d\sigma^*)$. The rupture of metal-ligand bonds would open the structures of the complexes and enhance the reactivity of complexes in the ³MC state, leading to the detrimental degradation process. Nevertheless, the intrinsic intramolecular π - π stacking has been proved to be a feasible way to enhancing the stability of LECs, which can restrict the opening of the structure in the ${}^{3}MC$ state effectively. In addition to the high quantum efficiency and reversible redox processes, these complexes as displayed in the crystal structures exhibit robust intramolecular π - π interactions. To evaluate the stability of the complexes, the ³MC states of them have been performed using the similar methodology illustrated in the reported works. The key bond lengths between iridium atom and N atom of cyclometalated ligands of the complexes in ³MC states have been determined and marked in Fig. 6. As shown in Fig. S4, the Ir–N bond (R1) of complex 1, of which N atom is in cyclometalated ligand bearing intramolecular π - π stacking with ancillary ligand, only lengthens from 2.08 Å in ground states (S₀) to 2.17 Å in the ³MC state. In contrast, electron promotion results in the elongation of another Ir-N length (R2), from 2.08 Å in S_0 state to 2.49 Å in the ³MC state for 1, leading to the virtual decoordination. Similar phenomenon are also observed in complexes 2–5. This indicates that the opening of the structure of the complex in the ${}^{3}MC$ state for these complexes 1–5 are effectively restricted due to the robust intramolecular π - π interactions, and the complexes studied here will be attractive materials for LECs. The relevant work on this aspect is

underway in our laboratory.

4. Conclusion

In summary, a series of multifunctional cationic iridium(III) complexes with different length of alkyl chains have been successfully synthesized. They all undergo remarkable and reversible PCL behavior, and the emission color can be switched upon grinding and heating. Moreover, their PCL properties are chain length-dependent, showing that the complex with shorter alkyl chain possesses more remarkable PCL behavior. The simple adjustment of the length of N-alkyl chains of piezochromic iridium(III) complexes with triazole-pyridine ligand could endow them with tunable solid-state emission and thermodynamics properties. The transformation between crystalline and amorphous states is found to be the main reason for the present piezochromism by carefully analyzing the experimental data (PXRD and DSC). The photophysical properties in solutions and neat films demonstrate that introducing different alkyl chains into the complexes has a little effect on their emitting colors and excited-state characters, which are supported by the theoretical calculations. Furthermore, the high quantum yields in neat films, excellent redox reversibility as well as the robust intramolecual π - π interactions that effectively restrict the opening of the structures in ³MC states, suggest that they would be promising candidates for applications in LECs. The results obtained here will help researchers to further design and synthesize more promising iridium(III)-based PCL materials and attractive phosphors for LECs.

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Figure captions

Scheme 1. Synthetic procedure and the chemical structures of complexes 1–5.

Fig. 1. Crystal structures of complexes 1 (a) and 2 (b). Thermal ellipsoids are drawn

at 30% probability. The PF_6 counter-anion and hydrogen atoms are omitted for clarity.

Fig. 2. Emission spectra of complexes 1 and 5 in the solid states. The letters "a" and

"g" represent as-synthesized and ground samples, respectively.

Fig. 3. PXRD patterns of as-synthesized samples 1a and 2a and ground samples 1g and 2g.

Fig. 4. DSC curves of as-synthesized samples (a) and ground samples (b).

Fig. 5. Absorption and emission spectra of complexes 1–5 in CH₃CN solution with concentration of 1×10^{-5} M at room temperature (a) and 77 K (b).

Fig. 6. The minimum-energy structure calculated for the ³MC state of complex **1**.



Scheme 1. Synthetic procedure and the chemical structures of complexes 1–5.



Fig. 1. Crystal structures of complexes 1 (a) and 2 (b). Thermal ellipsoids are drawn at 30% probability. The PF_6 counter-anion and hydrogen atoms are omitted for clarity.



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Fig. 3. PXRD patterns of as-synthesized samples 1a and 2a and ground samples 1g and 2g.



Fig. 4. DSC curves of as-synthesized samples (a) and ground samples (b).



Fig. 5. Absorption and emission spectra of complexes 1-5 in CH₃CN solution with concentration of 1×10^{-5} M at room temperature (a) and 77 K (b).

7 74	complex	R1 (Å)	R2 (Å)
	1	2.17	2.49
R2	2	2.18	2.50
	3	2.18	2.50
R1	4	2.19	2.52
	5	2.19	2.52

Fig. 6. The minimum-energy structure calculated for the ³MC state of complex **1**.

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checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report **Datablock: 55** Bond precision: C-C = 0.0226 AWavelength=0.71069 Cell: a=15.743(5) b=23.933(5) c=19.126(5)alpha=90 beta=90.000(5) gamma=90 293 K Temperature: Calculated Reported Volume 7206(3) 7206(3) Space group P 21/c P2(1)/c Hall group -P 2ybc ? C32 H22 F4 Ir N8, F6 P, C C33 H22 Cl2 F10 Ir N8 P Moiety formula C12 Sum formula C33 H22 Cl2 F10 Ir N8 P C33 H22 Cl2 F10 Ir N8 P 1014.66 1014.68 Mr 1.871 1.870 Dx,g cm-3 8 8 Ζ Mu (mm-1) 3.989 3.989 F000 3936.0 3936.0 F000′ 3929.87 h,k,lmax 18,28,22 18,28,22 Nref 12681 12651 0.330,0.433 Tmin,Tmax 0.328,0.435 Tmin' 0.291 Correction method= MULTI-SCAN Data completeness= 0.998 Theta(max) = 25.000R(reflections) = 0.0613(6142)wR2(reflections) = 0.1684(12651) S = 0.991Npar= 985

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**. Click on the hyperlinks for more details of the test.

🔍 Alert level B

SYMMS02_ALERT_1_BAll angles should not be 90 for a monoclinic cellCell15.743023.933019.1260Angles90.000090.000090.0000PLAT181_ALERT_1_BAll angles exactly 90 degrees in monoclinic cell? CheckPLAT342_ALERT_3_BLow Bond Precision onC-C Bonds0.0226 Ang.

🏓 Alert level C

PLAT026_ALERT_3_C	Ratio	Observed /	/ Unique	e Reflecti	lons	s too Low .			49	010
PLAT202_ALERT_3_C	Isotro	opic non-H	Atoms :	in Anion/S	Solv	vent			1	
PLAT214_ALERT_2_C	Atom F	717 (Ar	nion/Sol	lvent) ADE	e ma	ax/min Rati	io		4.2	prola
PLAT234_ALERT_4_C	Large	Hirshfeld	Differe	ence Irl	-	C10			0.16	Ang.
PLAT234_ALERT_4_C	Large	Hirshfeld	Differe	ence Cl	-	C6			0.20	Ang.
PLAT234_ALERT_4_C	Large	Hirshfeld	Differe	ence C3	-	C4	• •		0.22	Ang.
PLAT234_ALERT_4_C	Large	Hirshfeld	Differe	ence N15	-	C56			0.16	Ang.
PLAT234_ALERT_4_C	Large	Hirshfeld	Differe	ence C41	-	C42			0.16	Ang.
PLAT241_ALERT_2_C	Check	High	Ueq as	Compared	to	Neighbors	for		N7	
PLAT241_ALERT_2_C	Check	High	Ueq as	Compared	to	Neighbors	for		C4	
PLAT241_ALERT_2_C	Check	High	Ueq as	Compared	to	Neighbors	for)	C8	
PLAT241_ALERT_2_C	Check	High	Ueq as	Compared	to	Neighbors	for		C16	
PLAT242_ALERT_2_C	Check	Low	Ueq as	Compared	to	Neighbors	for		C5	
PLAT242_ALERT_2_C	Check	Low	Ueq as	Compared	to	Neighbors	for		N16	
PLAT243_ALERT_4_C	High	'Solvent'	Ueq as	Compared	to	Neighbors	of		Cl1	
PLAT244_ALERT_4_C	Low	'Solvent'	Ueq as	Compared	to	Neighbors	of		P1	
PLAT244_ALERT_4_C	Low	'Solvent'	Ueq as	Compared	to	Neighbors	of		P2	
PLAT244_ALERT_4_C	Low	'Solvent'	Ueq as	Compared	to	Neighbors	of		C01	
PLAT334_ALERT_2_C	Small	Average Be	enzene	C-C Dist.	. C4	41 -C46			1.37	Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite	6	
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms	3	
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF	?	Do !
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ	?	Check
PLAT112_ALERT_2_G ADDSYM Detects Additional (Pseudo) Symm. Elem	n	
PLAT112_ALERT_2_G ADDSYM Detects Additional (Pseudo) Symm. Elem	a	
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New Space-group.	Pbcn	
PLAT153_ALERT_1_G The su's on the Cell Axes are Equal	0.00500	Ang.
PLAT199_ALERT_1_G Check the Reported _cell_measurement_temperature	293	K
PLAT200_ALERT_1_G Check the Reporteddiffrn_ambient_temperature	293	K
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of	C02	
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder	5	00
PLAT344_ALERT_2_G Check Angle Range in Solvent/Ion for	C01	
PLAT380_ALERT_4_G Check Incorrectly? Oriented X(sp2)-Methyl Moiety	C63	
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels	3	
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF #	303	
C02 -CL1 -C02' 1.555 1.555 1.555	25.30 Deg.	
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. #	5	
C C12		
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints	24	

0 ALERT level A = Most likely a serious problem - resolve or explain 3 ALERT level B = A potentially serious problem, consider carefully 19 ALERT level C = Check. Ensure it is not caused by an omission or oversight 18 ALERT level G = General information/check it is not something unexpected 6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

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ACCEPTED MANUSCRIPT

14 ALERT type 2 Indicator that the structure model may be wrong or deficient

4 ALERT type 3 Indicator that the structure quality may be low

15 ALERT type 4 Improvement, methodology, query or suggestion

1 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 01/06/2013; check.def file version of 24/05/2013



CRA CRAN

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 11

Bond precision:	C-C = 0.0085 A	.71069		
Cell:	a=9.477(5)	b=16.602(5) c	=22.635(5)
	alpha=90	beta=95.37	4(5) g	amma=90
Temperature:	293 К			
TT = 1 =			Reported	
Volume	3546(2)		3546(2)	
Space group	P 21/C		P2(1)/C	
Hall group	-P ZYDC			T 110 D
Molety formula	C34 H26 F4 Ir N8	, F6 P	C34 H26 F10	Ir N8 P
Sum formula	C34 H26 F10 Ir N	8 P	C34 H26 F10	Ir N8 P
Mr	959.82		959.80	
Dx,g cm-3	1.798		1.798	
Z	4		4	
Mu (mm-1)	3.902		3.902	
F000	1872.0		1872.0	
F000'	1867.74)		
h,k,lmax	12,21,29		12,21,29	
Nref	8145		8093	
Tmin,Tmax	0.349,0.458		0.347,0.460	
Tmin'	0.322			
Correction metho	od= MULTI-SCAN			
Data completenes	ss= 0.994	Theta(ma	(x) = 27.500	
C				
R(reflections)=	0.0349(6270)	wR2(refl	ections) = 0	.0890(8093)
S = 1.022	Npar=	487		

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

🞈 Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for C32 -- C33 .. 7.9 su

Alert level C

PLAT147_ALERT_1_C su on Symmetry Constrained Cell Angle(s)	? Check
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min)	3.5 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C33 C34	0.21 Ang.
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of	Pl
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor	2.8
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds	0.0085 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C33 - C34	1.39 Ang.
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .	36 Ang3

Alert level G

PLATOU5_ALERT_5_G No _iucr_refine_instr	uctions_details	in the CLF	2	Do !
PLAT042_ALERT_1_G Calc. and Reported Mo	ietyFormula Str	ings Differ	?	Check
PLAT153_ALERT_1_G The su's on the Cell	Axes are Equa	1	0.00500	Ang.
PLAT199_ALERT_1_G Check the Reported _c	ell_measurement_	_temperature	293	K
PLAT200_ALERT_1_G Check the Reported	_diffrn_ambient	_temperature	293	K
PLAT231_ALERT_4_G Hirshfeld Test (Solve	nt) P1	F7	5.6	su
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	105	
C11 -C10 -IR1 -N5 110.00	0.90 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	106	
C15 -C10 -IR1 -N5 -67.60	1.10 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	117	
C6 -C1 -IR1 -N6 -119.00	4.00 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	118	
C2 -C1 -IR1 -N6 65.00	4.00 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	123	
C18 -N3 -IR1 -N1 122.00	1.10 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	124	
N4 -N3 -IR1 -N1 -54.30	1.20 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	133	
C9 -N1 -IR1 -N3 149.90	1.00 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	134	
N2 -N1 -IR1 -N3 -29.70	1.30 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	141	
C19 -N6 -IR1 -C1 -151.00	4.00 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	142	
C23 -N6 -IR1 -C1 17.00	4.00 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	157	
C10 -IR1 -N5 -C24 -8.60	1.10 1.555	1.555 1.555	1.555	
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4	Linear Torsion	Angle #	162	
C10 -IR1 -N5 -C25 176.20	0.80 1.555	1.555 1.555	1.555	

0 ALERT level A = Most likely a serious problem - resolve or explain 1 ALERT level B = A potentially serious problem, consider carefully 8 ALERT level C = Check. Ensure it is not caused by an omission or oversight 18 ALERT level G = General information/check it is not something unexpected 5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data 5 ALERT type 2 Indicator that the structure model may be wrong or deficient 1 ALERT type 3 Indicator that the structure quality may be low 15 ALERT type 4 Improvement, methodology, query or suggestion 1 ALERT type 5 Informative message, check It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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PLATON version of 01/06/2013; check.def file version of 24/05/2013



	$\lambda_{\rm em}$ (nm)	$ au_{I}$ ^[a]	$A_1^{[b]}$	$ au_2{}^{[a]}$	$A_2^{[b]}$	<\mathcal{t}>^{[c]}	$T_{cry}(^{\circ}C)^{[u]}$
1a	466	1.06	15.07	1.96	84.93	1.82	
1g	483	0.83	40.26	1.63	59.74	1.31	194.4
2a	463	0.67	30.52	1.18	69.48	1.02	
2g	483	0.60	34.07	1.38	65.93	1.11	163.2
3a	461	1.29	83.83	2.22	16.17	1.44	-
3g	483	0.91	42.80	1.55	57.20	1.28	136.1
4a	472	0.77	10.43	1.60	89.57	1.51	-
4 g	482	0.85	32.13	1.54	67.87	1.32	124.9
5a	465	0.70	8.19	1.53	91.81	1.46	-
5g	473	1.04	45.15	1.66	54.85	1.38	101.7

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Table 1Solid-state photophysical data and DSC results of complexes 1–5 in various

^aExcited-state lifetime.

states

^b Fractional contribution.

^c Weighted lifetime.

^d Crystallization temperature

	Room temperature emission			Emission at 77 K ^[a]	Electrochemical data ^[a]		
	$\lambda_{\rm em}({\rm nm})$	$\tau(\mu s)$	PLQY	$\lambda_{\rm em}({\rm nm})$	$\mathrm{E_{ox}}^{1/2}\left(\mathrm{V}\right)$	E _{red} ^{1/2} (V)	
1	504	0.33	57.6%	466	1.25	-1.80	
2	505	0.23	56.8%	461	1.24	-1.81	
3	505	0.33	54.9%	461	1.23	-1.82	
4	505	0.42	61.1%	463	1.23	-1.83	
5	505	0.80	65.3%	464	1.23	-1.82	

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 Table 2. Photophysical and electrochemical properties of complexes 1–5

^a Measured in CH₃CN solutions.

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