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#### Introduction

Stimuli-responsive materials with specific optical properties that can be tuned and controlled by external stimuli are attracting enormous attention for their potential applications in dynamic functional materials.<sup>1</sup> These materials are considered to be smart materials because their properties can be modified by external conditions, including pressure, temperature, light and electricity.<sup>2</sup> In particular, the newly developed piezochromic luminescent (PCL) materials exhibiting vivid and reversible changes of luminescence in the solid state without any chemical transformations have been the object of intense research efforts driven by their potential widespread applications ranging from sensors, and data storage, to security ink for optoelectronic devices.<sup>3</sup> One common strategy for altering the luminescence of PCL materials is to change the morphology of

# Effect of alkyl chain length on piezochromic luminescence of iridium(III)-based phosphors adopting 2-phenyl-1*H*-benzoimidazole type ligands<sup>†</sup>

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In this work, a series of luminescent cationic iridium(III) complexes containing 2-phenyl-1*H*-benzimidazoletype ligands modified with *n*-alkyl chains of various lengths have been successfully synthesized and characterized. Their photophysical and electrochemical properties have been investigated in detail. Differences in *n*-alkyl chain length has negligible affect on their respective complex's emission spectra or on their excited-state characteristics in solution, which is supported by density functional theory calculations and cyclic voltammetry. In the solid state, these complexes exhibit piezochromic luminescence (PCL) behaviour which is visible to the naked eye. Their emission colour can be reversibly and quickly switched by grinding–fuming or grinding–heating processes with high contrast. Moreover, the *n*-alkyl chain lengths can effectively control their PCL and thermodynamic properties, showing chain length dependent emission behaviours: longer alkyl chains were shown to produce more marked mechanochromism. A reproducible and reversible two-colour emission writing/erasing process was achieved by employing the iridium(III) materials as a medium. Powder X-ray diffractometry and differential scanning calorimetric studies suggest that the reversible transformation between crystalline and amorphous states upon application of external stimuli is responsible for the observed piezochromism.

> molecular aggregates. Such a change can be accomplished, for example, by changing the packing mode of the molecules in crystals or by promoting a phase transition from crystalline to amorphous states.<sup>4</sup> To date, a few PCL materials based on inorganic complexes, liquid crystal materials, gels, and polymer-based assemblies have been successfully developed.<sup>5</sup> However, the investigation of PCL materials is still in the initial stage, especially for metal-containing complexes.<sup>6</sup> The controllable design and synthesis of excellent PCL materials are difficult to achieve because of the lack of well-understood relationships between the structures of materials and their properties. Consequently, it remains a great challenge to design new PCL materials and explore the relationship between molecular packing and piezochromic behaviour.

> Organometallic iridium(m) complexes are regarded as promising candidates as triplet emitters in optoelectronic applications because of their high phosphorescence efficiency and superior optical stability as well as full-colour emission.<sup>7</sup> More recently, Huang *et al.*,<sup>8d</sup> Talarico *et al.*<sup>8a,8c</sup> and our group have developed a series of phosphorescent iridium(m) complexes with interesting piezochromism.<sup>8</sup> In addition, inspired by facile modification of the structures of iridium(m) complexes, we also realized the first example of these complexes simultaneously showing PCL and aggregation-induced

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<sup>†</sup> Electronic supplementary information (ESI) available: Computational details, synthesis and characterisation of complexes 1–3, and corresponding photophysical results. See DOI: 10.1039/c4tc00993b

emission behaviors.<sup>9</sup> Despite these advances, the design of iridium(III) complexes with PCL characteristics still remains a great challenge because of the reasons mentioned previously. Recent work has shown that introducing different long alkyl chains into the organic fluorescent PCL materials is an effective approach to constructing new PCL materials and for studying the relationship between the molecular structure and the PCL behavior.<sup>4c,10</sup> Following this design strategy, we developed a new set of comparable molecular cationic iridium(III) complexes with different *n*-alkyl chain lengths on the ancillary ligand.<sup>11</sup> The resulting iridium(III) complexes exhibited reversible PCL behaviour, but only the complex with the shortest *n*-alkyl chain, namely the methyl group, showed significant PCL, which limits the further optimization.

In our continuing pursuit of effective iridium(III)-based PCL phosphors, we have speculated that they can be designed in a different way, that is, to synthesize the iridium(III) complexes with different alkyl chains on cyclometalated ligands. Can these complexes also exhibit PCL behaviour and what is the relationship between chain length and PCL properties? Keeping these questions in mind, in the current work, a new series of cationic iridium(m) complexes with different n-alkyl chain lengths on the cyclometalated ligands were designed and successfully synthesized (see Scheme 1). According to their solid-state emissions, these complexes show PCL behaviour that can be adjusted by changing the *n*-alkyl chain lengths. The iridium(III) complex containing longer alkyl chains on the cyclometalated ligand exhibits a more marked PCL and a redshifted emission but a lower recrystallization temperature. The original emission colour can be recovered by heating or organic solvent fuming. To further understand the PCL mechanism, powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC) and excited-state lifetimes of the original and mechanically ground forms of the complex have been studied. The results obtained will help us to shed new light on the relationship between the chain length and the PCL behaviour of iridium(III) complexes and further develop more effective iridium(III)-based PCL materials.

### **Experimental section**

#### General information and materials

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. Thermogravimetric (TG) analyses were performed on a PerkinElmer TG-7 analyzer from 30 to 800 °C in flowing nitrogen at a heating rate of 10 °C min<sup>-1</sup>. PXRD patterns of the samples were collected on a Rigaku D/Max 2000. <sup>1</sup>H-NMR spectra were measured on Bruker Avance 500 MHz with tetramethylsilane as the internal standard. The molecular weights of ligands and complexes were determined by using electrospray-ionization mass spectroscopy (MS) and matrix-assisted laser desorption-ionization time-offlight (MALDI-TOF) MS, respectively. The emission spectra were recorded using an Hitachi F-4600 fluorescence spectrophotometer. The excited-state lifetimes were measured on an FLS920 transient spectrofluorimeter (Edinburgh Instruments) using time-correlated single-photon counting.

#### Synthesis

The cyclometalated ligands were easily prepared by reacting of 2-phenyl-1*H*-benzo[*d*]imidazole with the corresponding alkylogen in strongly basic conditions. Simple heating of a mixture of the dimeric iridium(III) intermediates and the ancillary ligands in dichloromethane/methanol (2 : 1 v/v) followed by counterion exchange produced the target complexes with moderate yields (50–70%). All complexes were fully characterized by using <sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectrometry as well as MALDI-TOF mass spectrometry.

#### Synthesis of the cyclometalated ligands

*Ethyl-2-phenyl-1H-benzo[d]imidazole (L1).* The precursor 2-phenyl-1*H*-benzo[*d*]imidazole (PhBI) was synthesized using a previously reported procedure.<sup>12</sup> Under a nitrogen atmosphere, PhBI (1.12 g, 5.8 mmol) was dissolved in acetone. An equivalent amount of KOH was added and the mixture was stirred for



Scheme 1 Synthetic routes and structures of iridium(III) complexes 1-5

30 min, followed by addition of bromoethane. After cooling to room temperature, the reactant mixture was heated to reflux overnight and quenched with ice water. The mixture was then extracted by dichloromethane (3 × 30 mL). The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. The product was then obtained by column chromatography on silica gel with ethyl acetate/petroleum (1 : 3) as the eluent to produce a light-yellow solid with a yield of 64%. <sup>1</sup>H-NMR (500 MHz, deuterated chloroform (CDCl<sub>3</sub>), ppm):  $\delta$  7.83– 7.85 (m, 1H), 7.72–7.73 (m, 2H), 7.51–7.53 (m, 3H), 7.42 (t, *J* = 4.5 Hz, 1H), 7.30–7.32 (m, 2H), 4.25–4.29 (m, 2H), 1.44 (t, *J* = 7 Hz, 3H). The related cyclometalated ligands (L2, L3, L4 and L5) were prepared using similar procedures.

Butyl-2-phenyl-1H-benzo[d]imidazole (L2). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.83–7.85 (m, 1H), 7.70–7.72 (m, 2H), 7.51–7.53 (m, 3H), 7.41 (t, *J* = 4.5 Hz, 1H), 7.30–7.32 (m, 2H), 4.21 (t, *J* = 7.5 Hz, 2H), 1.78 (t, *J* = 7.5 Hz, 2H), 1.24–1.29 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H).

*Hexyl-2-phenyl-1H-benzo[d]imidazole (L3).* <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.83–7.85 (m, 1H), 7.70–7.72 (m, 2H), 7.51–7.53 (m, 3H), 7.40 (t, *J* = 4.5 Hz, 1H), 7.29–7.31 (m, 2H), 4.19 (t, *J* = 7.5 Hz, 2H), 1.79 (t, *J* = 7.0 Hz, 2H), 1.21–1.24 (m, 6H), 0.84 (t, *J* = 6.5 Hz, 3H).

Octyl-2-phenyl-1H-benzo[d]imidazole (L4). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.83–7.84 (m, 1H), 7.70–7.71 (m, 2H), 7.50–7.51 (m, 3H), 7.41 (t, *J* = 3.0 Hz, 1H), 7.29–7.31 (m, 2H), 4.19 (t, *J* = 7.5 Hz, 2H), 1.78 (t, *J* = 7 Hz, 2H), 1.19–1.27 (m, 10H), 0.84 (t, *J* = 6.5 Hz, 3H).

1-decyl-2-phenyl-1H-benzo[d]imidazole (L5). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.81–7.82 (m, 1H), 7.64–7.66 (m, 2H), 7.41–7.46 (m, 3H), 7.32–7.34 (m, 1H), 7.23–7.26 (m, 2H), 4.12 (t, J = 7.5 Hz, 2H), 1.72–1.74 (m, 2H), 1.16–1.27 (m, 14H), 0.85 (t, J = 7 Hz, 3H).

Synthesis of the ancillary ligand. 2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl) pyridine (Phtz) was synthesized according to previously reported procedures, which produced a white solid with a yield of 75%. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.51 (d, *J* = 4.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.42–7.49 (m, 8H), 7.30 (t, *J* = 6 Hz, 1H).

Synthesis of the chloro-bridged dimer. The organometallated dimer  $[Ir(L1)_2Cl]_2$  was synthesized by reacting  $IrCl_3 \cdot 3H_2O$  (0.505 g, 1.43 mmol) with 1-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (L1; 0.656 g, 3.15 mmol) in a 2-ethoxyethanol and water mixture (3 : 1 v/v, 30 mL) for 24 h. The product was filtered out and washed with diethyl ether followed by ethanol, and dried (yield: 76%). Other chloride-bridged complexes,  $[Ir(L2)_2Cl]_2$ ,  $[Ir(L3)_2Cl]_2$ ,  $[Ir(L4)_2Cl]_2$  and  $[Ir(L5)_2Cl]_2$ , were synthesized using a method similar to that for  $[Ir(L1)_2Cl]_2$ . The chloro-bridged dimers were used in the subsequent reactions without further purification.

#### Synthesis and characterization of complexes 1-5

Synthesis and characterization of complex 1. A solution of ancillary ligand (0.172 g, 0.63 mmol) and the dichloro-bridged diiridium complex  $[Ir(L1)_2Cl]_2$  (0.386 g, 0.3 mmol) in a mixture of methanol (15 mL) and dichloromethane (30 mL) was refluxed for 24 h in the dark. After cooling to room temperature, the mixture was filtered, and then an excess of solid KPF<sub>6</sub> was added and the mixture was stirred for another 0.5 h at room

temperature. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane/ethyl acetate (6:1) and the resulting powders were recrystallized from the dichloromethane and petroleum ether mixture to give complex 1 as a light-yellow solid with a yield of 58%. <sup>1</sup>H-NMR (500 MHz, deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>), ppm):  $\delta$  8.08 (t, J =7.5 Hz, 1H), 7.98 (d, I = 7.5 Hz, 1H), 7.94 (d, I = 4.5 Hz, 1H), 7.90 (d, J = 7.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.71-7.78 (m, 3H),7.65 (t, J = 7.0 Hz, 1H), 7.35–7.45 (m, 4H), 7.24–7.31 (m, 5H), 7.13–7.17 (m, 2H), 7.04–7.09 (m, 2H), 6.85 (t, J = 8.0 Hz, 2H), 6.77 (t, J = 7.0 Hz, 1H), 6.70 (t, J = 7.0 Hz, 1H), 6.61 (t, J = 7.0 Hz, 1H), 6.26 (d, J = 8.0 Hz, 1H), 5.96 (d, J = 8.0 Hz, 1H), 5.87 (d, J =8.0 Hz, 1H), 4.93-4.95 (m, 2H), 4.66-4.71 (m, 1H), 4.55-4.60 (m, 1H), 1.52 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 6.5 Hz, 5H). <sup>19</sup>F-NMR (470 MHz, DMSO-d<sub>6</sub>, ppm): -67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 933.3 (M-PF<sub>6</sub>). The related complexes 2, 3, 4 and 5 were prepared using similar procedures.

Synthesis and characterization of complex 2. Light-yellow solid, (yield: 67%). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  8.06 (t, J = 8.0 Hz, 1H), 7.97 (d, J = 7.0 Hz, 1H), 7.91 (t, J = 5.0 Hz, 1H), 7.90 (s, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.71–7.78 (m, 3H), 7.65 (t, J = 7.0 Hz, 1H), 7.46 (d, J = 7.0 Hz, 2H), 7.35–7.41 (m, 2H), 7.23–7.33 (m, 5H), 7.12–7.18 (m, 2H), 7.05 (t, J = 7.0 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 7.5 Hz, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.58 (t, J = 8.0 Hz, 1H), 6.21 (d, J = 8.0 Hz, 1H), 5.98 (d, J = 7.5 Hz, 1H), 5.87 (d, J = 8.5 Hz, 1H), 4.86–4.97 (m, 2H), 4.65–4.68 (m, 1H), 4.53–4.59 (m, 1H), 1.90 (t, J = 7.0 Hz, 2H), 1.55 (t, J = 7.5 Hz, 2H), 1.26–1.39 (m, 4H), 0.89 (t, J = 7.11.11 Hz, 6F). MS (MALDI-TOF): m/z 989.4 (M–PF<sub>6</sub>).

Synthesis and characterization of complex 3. Light-yellow solid, (yield: 52%). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  8.08 (t, J = 8.0 Hz, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.91–7.94 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.72–7.80 (m, 3H), 7.66 (t, J = 6.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 2H), 7.37–7.43 (m, 2H), 7.24–7.33 (m, 5H), 7.13–7.19 (m, 2H), 7.06 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.86 (t, J = 7.5 Hz, 2H), 6.76 (t, J = 7.5 Hz, 1H), 6.72 (t, J = 7.5 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 6.00 (d, J = 8.0 Hz, 1H), 5.87 (d, J = 8.0 Hz, 1H), 4.95–4.98 (m, 1H), 4.87–4.90 (m, 1H), 4.66–4.69 (m, 1H), 4.54–4.59 (m, 1H), 1.92 (t, J = 7.0 Hz, 2H), 1.58 (s, 2H), 1.19–1.38 (m, 12H), 0.78–0.84 (m, 6H). <sup>19</sup>F-NMR (470 MHz, DMSO-d6, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 1045.3 (M–PF<sub>6</sub>).

Synthesis and characterization of complex 4. Yellow-green solid, (yield: 76%). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  8.07 (t, J = 7.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.89–7.92 (m, 2H), 7.84 (d, J = 7.5 Hz, 1H), 7.71–7.78 (m, 3H), 7.64 (t, J = 6.5 Hz, 1H), 7.43 (d, J = 7.5 Hz, 2H), 7.35–7.41 (m, 2H), 7.22–7.31 (m, 5H), 7.11–7.17 (m, 2H), 7.04 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 7.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 6.70 (t, J = 7.0 Hz, 1H), 6.56 (t, J = 7.5 Hz, 1H), 6.21 (d, J = 7.5 Hz, 1H), 5.98 (d, J = 8.0 Hz, 1H), 5.85 (d, J = 8.5 Hz, 1H), 4.94–4.97 (m, 1H), 4.86–4.89 (m, 1H), 4.64–4.67 (m, 1H), 4.54–4.57 (m, 1H), 1.92–1.93 (m, 2H), 1.58 (s, 2H), 1.17–1.36 (m, 20H), 0.79–0.82 (m, 6H). <sup>19</sup>F-NMR (470 MHz, DMSO-d<sub>6</sub>, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 1101.5 (M–PF<sub>6</sub>).

Synthesis and characterization of complex 5. Yellow-green solid, (yield: 82%). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  8.08 (t, J = 7.0 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.90–7.93 (m, 2H), 7.85 (d, J = 8.5 Hz, 1H), 7.72–7.78 (m, 2H), 7.66 (t, J = 6.5 Hz, 1H), 7.44 (d, J = 6.5 Hz, 2H), 7.36–7.43 (m, 2H), 7.24–7.33 (m, 6H), 7.12–7.18 (m, 2H), 7.05 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 7.5 Hz, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 6.22 (d, J = 7.5 Hz, 1H), 6.00 (d, J = 8.0 Hz, 1H), 5.86 (d, J = 8.5 Hz, 1H), 4.95–4.97 (m, 1H), 4.87–4.90 (m, 1H), 4.66–4.68 (m, 1H), 4.57–4.58 (m, 1H), 1.92–1.93 (m, 2H), 1.57 (s, 2H), 1.17–1.36 (m, 28H), 0.81–0.83 (m, 6H). <sup>19</sup>F-NMR (470 MHz, DMSO-d<sub>6</sub>, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 1157.6 (M–PF<sub>6</sub>).

#### Results and discussion

#### Photophysical and electrochemical properties in the solutions

The emission spectra of complexes 1-5 in CH<sub>3</sub>CN are shown in Fig. 1. They all exhibit almost identical emission profiles with peaks around 600 nm. Their broad and featureless emission spectra indicate that their emissive excited states have predominantly triplet metal-to-ligand charge-transfer (<sup>3</sup>MLCT) and triplet ligand-to-ligand charge-transfer (<sup>3</sup>LLCT) characteristics,13 which is further supported by density functional theory (DFT) calculations (see below). As shown in Fig. S1 (ESI<sup>+</sup>), the highest occupied molecular orbitals (HOMOs) of all complexes are mainly located on the cyclometalated ligands and the iridium ion, while the lowest unoccupied molecular orbitals (LUMOs) reside on the ancillary ligands with no distribution on the pendant phenyl groups. The time-dependent density functional theory (TD-DFT) method was also performed to further understand the nature of the emissive excited states of complexes 1–5. The results show that the lowest-lying triplet  $(T_1)$ states of the complexes originate predominantly from the excitation of HOMO $\rightarrow$ LUMO (see Table S1, ESI<sup>+</sup>). Therefore, the T<sub>1</sub> states have predominantly mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  the ancillary ligands) and <sup>3</sup>LLCT (cyclometalated ligands  $\rightarrow$  the ancillary ligands) characteristics. The results were also confirmed by difference electron density calculations (Fig. S2, ESI<sup>†</sup>). In addition, the theoretical data demonstrate that the n-alkyl chain lengths introduced into cyclometalated ligands do not



Fig. 1 Emission spectra of solutions of complexes 1–5 in  $1\times 10^{-5}$  M  $CH_3CN$  at room temperature.



contribute to HOMOs and LUMOs, indicating that the different

*n*-alkyl chain lengths have little effect on their excited-state

switching to the reduction sweep in  $CH_3CN$ , one reversible reduction peak at -1.39 V *versus* Fc/Fc<sup>+</sup> was detected for each complex. As revealed by previous electrochemical studies and theoretical calculations, these reduction processes should occur on the ancillary ligands.<sup>15</sup> Considering that these complexes share nearly the same emission energy as well as similar electrochemical behaviour in solution, we propose that the different alkyl chain lengths have negligible influence on the photophysical properties of the complex as well as on their electrochemical behaviour. Furthermore, their redox reversibility indicates that both the holes (upon oxidation) and electrons (upon reduction) can be easily transported when they are employed as luminescent materials, which is beneficial for their application in optical devices.<sup>16</sup>

# Photophysical properties in the solid-state and piezochromic behaviour

It is known that the emission properties of luminophores depend strongly on the molecular arrangement motif and intermolecular interactions in solid-state.<sup>17</sup> To evaluate whether the functional *n*-alkyl chain lengths affect their solid-state emissions, the emission spectra of all the as-synthesized solid powders were measured and are shown in Fig. 2 (complexes 1 and 5) and Fig. S4.<sup>†</sup> The corresponding numerical data are summarized in Table 1. These iridium(III) complexes show bright emission colours at room temperature, ranging from yellow-greenish (557 nm) to green (528 nm). This variation is different from the emission spectra in the solution, which show almost identical emission profiles for all of the complexes (see Fig. 1). These observations indicate that the different *n*-alkyl chain lengths substantially affect the molecular packing in the solid state and thus, their optical properties. Therefore,



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

Table 1 Emission maximum ( $\lambda$ , in nm) and excited-state lifetimes ( $\tau$ , in  $\mu$ s) of as-synthesized and ground samples of complexes 1–5 as well as their thermal transition data in the ground state

Complex	$\lambda_{as-synthesized}$	$\lambda_{\mathrm{ground}}$	$\Delta \lambda_{ m PCL}{}^a$	$\tau_{\mathrm{as-synthesized}}$	$\tau_{\mathrm{ground}}$	T <sub>cry</sub> <sup>b</sup>
	-	-00	20	0.70	0.40	
1	560	588	28	0.78	0.49	244
2	550	584	34	0.93	0.52	182
3	547	582	35	0.93	0.54	186
4	534	578	44	1.03	0.64	175
5	528	575	47	1.25	0.77	138
$a \wedge \lambda = \lambda$ $b$ Crystallization temperature						

<sup>*a*</sup>  $\Delta \lambda_{PCL} = \lambda_{ground} - \lambda_{original}$ . <sup>*b*</sup> Crystallization temperature.

adjusting the *n*-alkyl chain lengths in a cyclometalated ligand is an effective way to control the emission for iridium(m) complexes in the solid-state.

In order to examine whether these iridium(m) complexes have PCL properties, mechanical grinding experiments on the as-synthesized powders (namely, 1a-5a), were carried out. Interestingly, after grinding each of the as-synthesized solid powders in an agate mortar with a pestle, an obvious visible emission can be seen by the naked eye. Additionally, this change occurred only at the pressed area (see Fig. S5<sup>†</sup>). Upon grinding sample 1a, the yellow-greenish powder with an emission maximum of 557 nm changed into an orange-emissive solid ( $\lambda_{em} = 588$  nm). Other samples also show similar significant PCL properties. Clearly, grinding induces a red shift of about 28-47 nm in the emission, i.e., from yellow-greenish and green luminescence to orange. Importantly, it is worth noting that the grinding-induced spectral shift ( $\Delta \lambda_{PCL}, \Delta \lambda_{PCL} = \lambda_{ground}$  $-\lambda_{as-synthesized}$ ) of these iridium(III) dyes are dependent on the length of the alkyl chain. As shown in Fig. 2, complex 5, with its long *n*-alkyl chain, exhibited a greater PCL shift ( $\Delta \lambda_{PCL} = 47 \text{ nm}$ ) than did complex 1 ( $\Delta \lambda_{PCL} = 31$  nm). The  $\Delta \lambda_{PCL}$  values for complexes 2, 3, and 4 are 34, 35 and 44 nm, respectively. These  $\Delta \lambda_{PCL}$  values are qualitatively consistent with the corresponding emission images shown in the inset of Fig. 2 and Fig. S4.†

Based on these results, we tentatively propose that the attachment of longer alkyl chains to the cyclometalated ligand may facilitate an effective PCL behaviour of cationic iridium(III) complexes. However, their alkyl length dependency is in contrast to our previous design strategy.11 In general, the PCL behavior of luminophores is related to the arrangement of their molecular motifs and their intermolecular interactions. The PCL materials with weak intermolecular interactions usually exhibit more significant PCL properties than those with strong ones.4c,10d,10f In our previous work, however, the case was different, probably because the alkyl chain was introduced into ancillary ligands.11 It appears that adding a long alkyl chain to a cyclometalated ligand can decrease the intermolecular interactions more effectively than it does by adding it to an ancillary ligand. These results provide a new structure-property relationship and material systems for further comparative studies.

The emission colours of all ground samples were found to be stable for more than one week at room temperature. However, upon exposure to organic solvent, the orange-emitting samples (ground samples) exhibited a visible blue-shifted emission. For

comparison, the photographs of the emission colours in different states of the samples are shown in Fig. 3. Upon solvent-fuming, not all of the emission profiles for the fumed samples exactly match those of the original unground one, and the hypsochromic shifts are observable to the naked eye. The corresponding emission spectra can be found in Fig. S6-S10.<sup>†</sup> In addition, upon adding a small quantity of diethyl ether to the ground samples, a blue shift of the emission can be immediately observed; this procedure, which has been infrequently reported for PCL materials, allows a fast reversal of the original change of color. In addition to solvent-fuming, the luminescent colours of ground samples of PCL materials can also be reversibly switched to the original colours by other environmental stimuli, such as heating.18 With this consideration in mind, the changes of emission colour during the grindingheating processes were studied. When heating the ground samples at appropriate temperatures, determined by the DSC data (see below), their emission colours changed from orange to yellow-greenish, by different degrees (see Fig. 3). Thus, the heating can also trigger the reversible changes in emission colour. Based on the previous results, it can be concluded that alkyl chains play a functional role in tuning the molecular packing in solid states as well as PCL reversibility induced by heating and/or solvent fuming. In this way, effective iridium(III)based PCL materials can be constructed by introducing an alkyl chain with an appropriate length into the cyclometalated ligand.

Reversible change in emission colour is an important feature for PCL materials in real-world applications. Therefore, the reversibility of the mechanochromic processes of complex 5 was investigated as an example. As shown in Fig. S11,† this complex shows good and stable reversibility for both grinding–heating and grinding–fuming cycles. To test the potential applications of PCL iridium(III) complexes in optical devices, complex 5 was chosen as the medium because of its relatively remarkable PCL behaviour and excellent reversibility. As shown in Fig. 4, when



Fig. 3 Luminescent images of complexes 1–5 in different states under a 365 nm UV lamp. Pristine represents as-synthesized samples.

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the as-prepared powder 5 is carefully smeared on a filter paper as a thin film and then subjected to solvent fuming, it emits a yellow-green light upon excitation with a UV lamp. The word "NENU" was written on this film using a spatula, and an orangeemitting pattern with large colour contrast is observed. Fuming the film with diethyl ether erases the letter and reinstalls the original yellow-green background. A new word "IFMC" can be re-written on the film and erased using the same method mentioned above. In this way, reversible colour-changing based on a PCL-active iridium(III) complex has been demonstrated, indicating its potential use as a recyclable optical storage medium.

To investigate the phosphorescence decay behaviour before and after grinding, the excited-state lifetimes of complexes 1-5 in various states were determined. The data are shown in Table 1. The excited-state lifetimes  $(\tau)$  for the as-synthesized samples are significantly different from those of ground samples: the grinding results in the evident decease of  $\tau$ . However, in the case of cationic iridium(III) complexes without PCL behaviour, the lifetimes of as-synthesized and ground sample are almost identical. Thus, the as-synthesized and ground samples of the same complex exhibit different time-resolved emission-decay behaviours, for which the fundamental cause is altering the mode of solid-state molecular packing and/or the intermolecular interactions after grinding. Their <sup>1</sup>H-NMR spectra in different states have been obtained as well. Almost no changes were found for these spectra in different states, further validating the fact that their emission colour changes are caused by physical processes during the grinding rather than by a chemical reaction.

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

The PCL behaviours of organic materials are usually related to the changes of the morphologies of their molecular aggregates, such as changes in the packing mode of molecules in a crystal or the phase transition between crystalline and amorphous states. To gain insight into the PCL mechanism of the iridium(III) complexes, namely complexes 1–5, PXRD data for assynthesized and ground samples were collected. As can be seen from Fig. 5, all as-synthesized samples produced sharp and



Fig. 4 Photographs of the reversible writing/erasing cycle using complex 5 as the medium.

relatively intense PXRD reflections, indicating that these original powders obtained after column chromatography are wellordered crystalline structures.19 In contrast, grinding the assynthesized samples leads to a broadening of the reflections and lowering of their intensities in the PXRD patterns, suggesting that amorphous states formed instead of the ordered structures.20 After heating or solvent fuming the ground samples, some sharp diffraction peaks appeared again (Fig. 5 and Fig. S12-S14, ESI<sup>†</sup>). Thus, crystalline structures formed upon heating or fuming, although the reflection peaks of the heated and solvent-fumed samples of complex 1 differ from those of the as-synthesized sample. These results thus suggest that heating or solvent fuming can convert amorphous ground samples to crystalline states through molecular repacking, and reversible interconversion of piezochromic luminescence can thus be achieved.

In addition to PXRD investigations, a DSC study was carried out to further confirm the amorphous nature of the powders formed upon grinding. As shown in Fig. 6, no endothermic and/ or exothermic peaks were detected before their melting point  $(T_m)$  for the as-synthesized samples. However, each ground sample features cold-crystallization temperatures before the  $T_m$ . It is known that amorphous solids become less viscous and the molecules may obtain enough freedom of motion to spontaneously arrange themselves into crystalline forms upon heating. Thus, based on combining the PXRD and DSC results, it appears that the ground samples investigated here are metastable amorphous states. If the ground samples are heated above their recrystallization temperatures or are subjected to solvent-fuming, they will restore to thermodynamically stable



Fig. 5 PXRD patterns of as-synthesized samples and corresponding ground samples.



Fig. 6 DSC curves of as-synthesized samples (A) and ground samples (B).

crystals through the recrystallization process. However, it was noticed that the recrystallization temperature of 5g, which has long alkyl chains, is lower than the recrystallization temperatures of 1g-4g, which may be attributed to the much weaker intermolecular interactions in 5g than in the others. The results show that the recrystallization temperatures for ground samples are also dependent on chain length: that is the longer the alkyl chains, the lower the recrystallization temperatures. It is possible that long alkyl chains are unfavourable for close packing of the molecules and endow the materials with low melting points and thermal transition temperatures. These findings are similar to those of recently reported PCL materials based on organic small molecules. Therefore, adjusting the nalkyl length of cationic iridium(III) complexes cannot only help design excellent PCL materials but also control their heatrecovery temperature.

#### Conclusions

In summary, we have designed and successfully synthesized a new class of cationic iridium(III) complexes with different n-alkyl chains in 2-phenyl-1H-benzoimidazole-type ligands. They show strong orange emissions with emission profiles in solutions that are independent of alkyl chain length, as well as excitedstate properties that are well characterized by spectroscopic techniques and theoretical calculations. Interestingly, upon grinding the solid powders, all complexes show PCL behaviours visible to the naked eye: their emissions can be repeatedly switched between green and yellow-orange colours by quick grinding-fuming or grinding-heating processes. Moreover, changing the lengths of the *n*-alkyl chains can effectively adjust their PCL behaviour and thermodynamic properties. The iridium(m) complex with longer *n*-alkyl chains shows larger grinding-induced spectral shifts, leading to more effective iridium(III)-based PCL materials. In view of the PXRD and DSC data, the interconversion between crystalline and amorphous states upon application of external stimuli is responsible for the observed piezochromism. The relationships between structure and PCL behaviour obtained in this research will be useful for developing and designing more promising iridium(m)-based piezochromic materials in the future.

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