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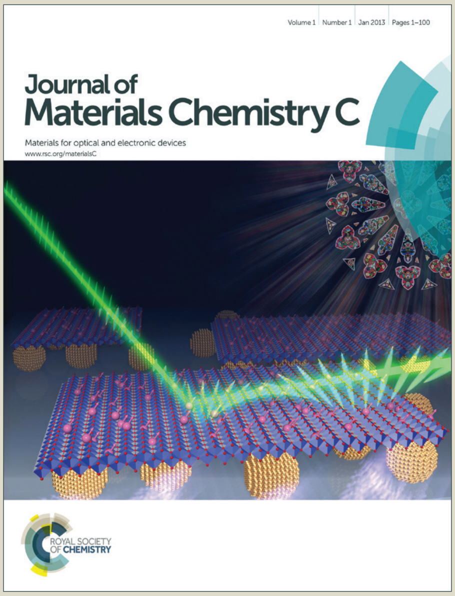

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PAPER

Alkyl chain length effects on piezochromic luminescence of iridium(III)-based phosphors adopting 2-phenyl-1*H*-benzoimidazole type ligands

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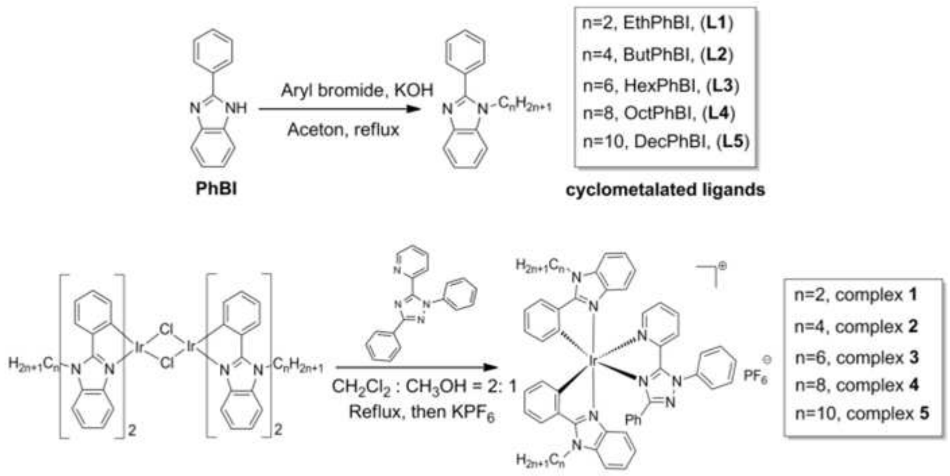
In this work, a series of luminescent cationic iridium(III) complexes containing 2-phenyl-1*H*-benzoimidazole type main ligands modified with various *N*-alkyl chain lengths have been successfully synthesized and characterized. The photophysical and electrochemical properties of them have been investigated in detail. The different *N*-alkyl chain lengths show the negligible effect on their emission spectra as well as the excited-state characteristics in solutions, which are supported by density functional theoretical (DFT) calculation and cyclic voltammetry study. In the solid states, they exhibit naked-eye visible piezochromic luminescence (PCL) behaviour. The emission of them can be reversibly and quickly switched by grinding-fuming or grinding-heating processes with a high contrast. Moreover, the *N*-alkyl chain lengths can effectively control their PCL and thermodynamics properties, showing the chain length-dependent emission behaviours: the longer the alkyl chain is, the more remarkable mechanochromism it will be. The reproducible and reversible two-colour emission writing/erasing process is 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 external stimuli is responsible for the present piezochromism.

Introduction

Stimuli-responsive materials with specific optical properties that can be tuned and controlled by external stimuli are attracting enormous attentions for their potential applications in dynamic functional materials.[1] Thanks to their distinctive properties which can be switched in environments or by the external conditions, including pressure, temperature, light and electricity, these materials are considered as smart materials.[2] In particular, the newly emerged piezochromic luminescent (PCL) materials exhibiting vivid and reversible luminescence change in the solid states but without chemical reactions have been the object of intense research effort driven by their widespread applications ranging from sensor, data storage, and security ink to optoelectronic devices.[3] For altering the luminescence of PCL materials, one common strategy is to alter the molecular aggregation morphology such as the packing mode of crystal molecules or the phase transition from crystalline to amorphous states.[4] To date, a few PCL materials based on inorganic complexes, liquid crystal materials, gel as well as polymer-based assemblies, have been successfully developed.[5] However, the investigation of PCL materials is still in the initial stage, especially for metal-contained complexes.[6] The controllable design and synthesis of excellent PCL materials are difficult to achieve due to the lack of clear structure-property relationship. Consequently, it remains a great challenge to design new PCL materials and explore the relationship between molecular packing and piezochromic behaviour.

Organometallic iridium(III) complexes are regarded as promising candidates for triplet emitters in optoelectronic applications owing to their high phosphorescence efficiency and superior optical stability as well as full colour emission.[7] More recently, Huang et al., Talarico et al. as well as our group have developed a series of phosphorescent iridium(III) complexes with the interesting piezochromism.[8] In addition, inspired by facile structural medication of iridium(III) complexes, we also realized the first example of iridium(III) complexes simultaneously showing PCL and aggregation-induced emission behaviors.[9] Despite these advance, the design of iridium(III) complexes with PCL characteristics still remains a great challenge due to the reasons as mentioned above. Recent works have been proved that introducing different long alkyl chains into the organic fluorescent PCL materials is an effective approach to construct new PCL materials and to study the relationship between the molecule structure and PCL behavior.[4c, 10] Following this design strategy, we have developed a new set of comparable molecular cationic iridium(III) complexes with different *N*-alkyl chain lengths on the ancillary ligand.[11] The resulting iridium(III) complexes exhibit reversible PCL behaviour. However, only the complex with short *N*-alkyl chain, namely methyl group, shows significant PCL feature, which limits the further optimization.

In our continuing pursuit of effective iridium(III)-based PCL phosphors, we conjecture whether they can be designed in an



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

opposite way, that is, to synthesis 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 in mind, in the current work, a new series of cationic iridium(III) complexes with different *N*-alkyl chain lengths on the cyclometalated ligands were designed and successfully synthesized (see scheme **1**). The investigations on their solid-state emissions demonstrate that all of them show the adjustable PCL behaviour *via* changing the *N*-alky chain lengths. The iridium(III) complex containing longer alky chains on cyclometalated ligand exhibit more significant PCL feature with red-shifted emission but lower recrystallization temperature. The changed emission colour can been recovered through heating or organic solvent fuming. To further understand the present PCL mechanism, the powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC) and excited-state lifetime in original and mechanical ground states have been studied. The obtained results herein will help us to cast 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. TG analyses were performed on a Perkin-Elmer TG-7 analyzer heated from 30 to 800 °C in flowing of nitrogen at the heating rate of 10 °C/min. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Dmax 2000. ^{1}H 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. The emission spectra were recorded using the F-4600 FL spectrophotometer. The excited-state lifetimes were measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photo counting technique.

Synthesis

The cyclometalated ligands were easily prepared by the reaction of 2-phenyl-1*H*-benzo[d]imidazole with corresponding alkylogen in the presence of the strong base condition. Simple heating the mixture of the dimeric iridium(III) intermediates and the ancillary ligands in the mixture dichloromethane/methanol (V : V = 2 : 1) and subsequent the counterion exchange reaction produced the target complexes with the moderate yields (50–70%). All complexes were fully characterized by ^{1}H NMR and ^{19}F NMR spectrometry as well as matrix-assisted laser desorption-ionization time-of-flight (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 by a previously reported procedure.[12] Under nitrogen atmosphere, PhBI (1.12 g, 5.8 mmol) was dissolved in acetone. Add the equivalent KOH and stir the mixture for 30 min. Then the bromoethane was added into the reaction mixture. After cooling to room temperature, the reactant was heated to reflux for overnight and quenched by ice water. After that, the mixture was extracted by dichloromethane (3×30 mL). The organic layer was dried with Na_2SO_4. 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 yield a light-yellow solid (64%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 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 the similar procedures.

Butyl-2-phenyl-1H-benzo[d]imidazole (L2)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 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)

^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 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)

^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 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)

^{1}H NMR (500 MHz, CDCl$_3$, 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. White-solid; (Yield: 75%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 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 and complexes 1–5

The organometallated dimer $[Ir(L1)_2Cl]_2$ was synthesized from reaction of $IrCl_3\cdot 3H_2O$ (0.505 g, 1.43 mmol) with 1-methyl-2-phenyl-1*H*-benzo[d]imidazole (L1 0.656 g, 3.15 mmol) in 2-ethoxyethanol and water mixture (V : V = 3:1, 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 $[Ir(L2)_2Cl]_2$. 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 the mix solution of methanol (15 mL) and dichloromethane (30 mL) was refluxed for 24 h in the dark. After cooling to room temperature, the mixture was filtrated, and then an excess of solid KPF_6 was added and 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 dichloromethane and petroleum ether mixture to give complex **1** as a light-yellow solid, (yield 58%). ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm): δ 8.08 (t, J = 7.5 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 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). ^{19}F NMR (470 MHz, d$_6$-DMSO, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 933.3 (M–PF$_6$). The related complexes **2**, **3**, **4** and **5** were prepared using the similar procedures.

Synthesis and characterization of complex 2

Light-yellow solid, (yield 67%). ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm): δ 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 = 7.5Hz, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.71 (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 = 7.0 Hz , 6H). ^{19}F NMR (470 MHz, d$_6$-DMSO, ppm): –67.30 (d, J = 711.11 Hz, 6F). MS (MALDI-TOF): m/z 989.4 (M–PF$_6$).

Synthesis and characterization of complex 3

Light-yellow solid, (yield 52%). ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm): δ 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 = 7.5Hz, 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). ^{19}F NMR (470 MHz, d$_6$-DMSO, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 1045.3 (M–PF$_6$).

Synthesis and characterization of complex 4

Yellow-green solid, (yield 76%). ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm): δ 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). ^{19}F NMR (470 MHz, d$_6$-DMSO, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 1101.5 (M–PF$_6$).

Synthesis and characterization of complex 5

Yellow-green solid, (yield 82%). ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm): δ 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). ^{19}F NMR (470 MHz, d$_6$-DMSO, ppm): –67.30 (d, J = 710.17 Hz, 6F). MS (MALDI-TOF): m/z 1157.6 (M–PF$_6$).

Results and discussion

Photophysical and electrochemical properties in the solution

The emission spectra of complexes **1**–**5** in CH_3CN solution were recorded and have been shown in Fig. 1. It is clear that all complexes exhibit almost identical emission profiles with peaks around 600 nm. The board and featureless emission spectra of them indicate that their emissive excited states have predominantly characters of ^{3}MLCT and ^{3}LLCT,[13] which is further supported by the density functional theoretical (DFT) calculations (*vide infra*). As shown in Fig. S1 (ESI†), the highest occupied molecular orbitals (HOMOs) of all complexes 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) approach 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→LUMO (See Table S1, ESI†). Accordingly, the T_1 states have predominantly characters of mixed ^{3}MLCT (Ir→the ancillary ligands) and ^{3}LLCT (cyclometalated ligands→the ancillary ligands). The results are also confirmed by the difference electron density calculations (Fig. S2, ESI†). In addition, the theoretical data demonstrate that the *N*-alkyl chain lengths introduced into cyclometalated ligands do not contribute to HOMOs and LUMOs, indicating the different *N*-alkyl chain lengths have little effects on their excited-state characters as well as emission colour in solution. This result is similar to the previous reports.[12, 14]

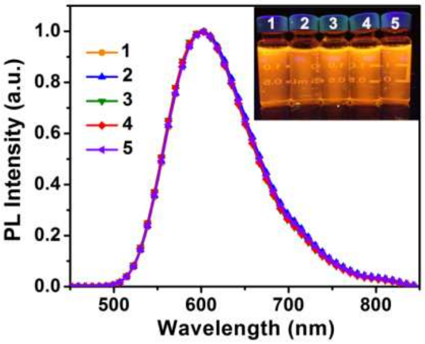


Fig. 1 Emission spectra of complexes **1**–**5** in CH_3CN solution with concentration of 1×10^{-5} M at room temperature.

The electrochemical behaviours of complexes **1**–**5** have been also investigated by cyclic voltammetry (CV) and the corresponding CV cures are displayed in Fig. S3†. The electrochemical data show that each complex exhibits a reversible redox processes in CH_3CN solution with oxidation peaks at +0.89 V versus Fc/Fc^+, which are assigned to the metal-centred Ir^{III}/Ir^{IV} couples. Upon switching to the reduction sweep in CH_3CN, one reversible reduction peaks at –1.39 V versus Fc/Fc^+ was detected for all of them. As revealed by previous electrochemical studies and theoretical calculations, these reduction processes should occur on the ancillary ligands.[15] Considering that they process almost identical emission energy as well as similar electrochemical behaviours in solution, it is thus proposed that different alkyl chains have neglectable influence on the photophysical properties of them and even their electrochemical behaviours. Furthermore, the redox reversibility of them indicates that both the holes (upon oxidation) and electrons (upon reduction) can be easily transported when employing them as luminescent materials, which is beneficial for the application in optical devices.[16]

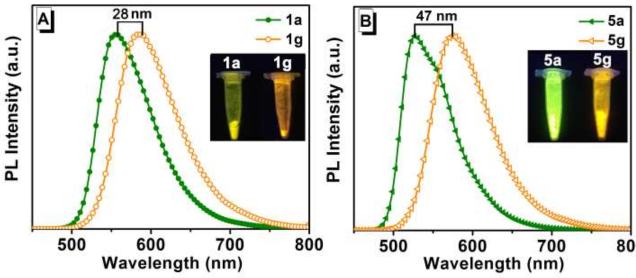


Fig. 2 Emission spectra of complexes **1** and **5** in the solid states. The letters "a" and "g" represent as-synthesized and ground samples, respectively.

Table 1. Emission maximum (λ, in nm) and excited-state lifetimes (τ, in μs) of as-synthesized and ground samples of complexes **1**–**5** as well as their thermal transition data in ground states.

complex	$\lambda_{\text{as-synthesized}}$	λ_{ground}	$\Delta\lambda_{\text{PCL}}$ [a]	$\tau_{\text{as-synthesized}}$	τ_{ground}	T_{cry} [b]
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] $\Delta\lambda_{\text{PCL}} = \lambda_{\text{ground}} - \lambda_{\text{original}}$

[b] Crystallization temperature

Photophysical properties in the solid-state and pizochromic behaviour

It is known that the emission properties of luminophors strongly depend on the molecular arrangement motif and intermolecular interactions in solid states.[17] To evaluate whether the functional *N*-alkyl chain lengths have effect on their solid emissions, the emission spectra of all as-synthesized solid powders were measured and shown in Fig. 2 (complexes **1** and **5**) and Fig. S4**†.** 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) emitting, respectively. Nevertheless, this is different from the emission spectra in the solution, which show almost identical emission profiles (see Fig. 1), indicating that the different *N*-alkyl chain lengths substantially affects the molecular packing in solid state and hence their optical property. Therefore, adjusting *N*-alky chain lengths in cyclometalated ligand is also an effective way to control the emission for iridium(III) complexes in the solid state. In order to examine whether these iridium(III) complexes have the PCL properties, the mechanical grinding experiments on the as-synthesized powders (namely, **1a**–**5a**), have been carried out. Interestingly, after grinding each as-synthesized solid powder in an agate mortar with a pestle, the obvious and naked-eye visible emission colour is observed. Additionally, this change occurred only at the pressed area (see

Fig. S5†). Upon grinding, for sample **1a** with emission maximum of 557 nm, the yellow-greenish powders changed into orange-emissive solid (λ_{em} = 588 nm). Other samples also undergo similar and significant PCL properties. Clearly, grinding induces the emission red shift of about 28–47 nm, respectively, i.e. from yellow-greenish and green luminescent colour to orange-emitting. Importantly, it is noteworthy that the grinding induced spectral shift ($\Delta\lambda_{PCL}$, $\Delta\lambda_{PCL} = \lambda_{ground} - \lambda_{as\text{-} synthesized}$) of these iridium(III) dyes are alkyl length-dependent. As shown in Fig. 2, complex **5** with the longer *N*-alky chain exhibit more remarkable PCL behaviour ($\Delta\lambda_{PCL}$ = 47 nm) compared with that of **1** ($\Delta\lambda_{PCL}$ = 31 nm). The $\Delta\lambda_{PCL}$ values for complexes **2**–**4** are 34, 35 and 44 nm, respectively. These $\Delta\lambda_{PCL}$ values are qualitatively consistent with the corresponding emission images observed in inset of Fig. 2 and Fig. S4†. Based on this result, we tentatively propose that attachment of longer alky chain at cyclometalated ligand may facilitate the effective PCL behaviours of cationic iridium(III) complexes. However, their alky length-dependency is in contrast to our previous design strategy.[11] In general, the PCL behaviors of luminophors are related to their molecular arrangement motifs and 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 the ancillary ligands.[11] It is believed that introducing long alkyl chain into cyclometalated ligand can decrease the intermolecular interactions more effectively than into ancillary ligands. These discoveries will provide new structure-property relationship and material systems for further comparable investigation.

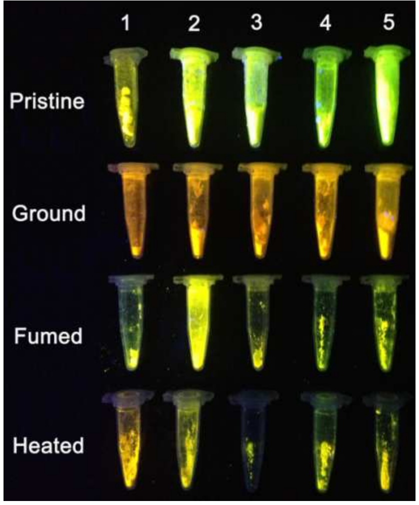


Fig. 3 Luminescent images of complexes **1-5** in various different states under 365 nm UV lamp. Pristine represents as-synthesized samples.

Furthermore, the emission colours of all ground samples were found to be stable more than one week at room temperature. However, upon exposure to organic solvent, the orange-emitting colour samples (ground samples) exhibit visible blue-shifted emission. For comparison, the emission colour photos in different states of the samples are revealed in Fig. 3. Upon solvent-fuming, although not all of the emission profiles for the fumed samples exactly match those of the original unground one, the naked-eye visible and hypsochromic shift emission colour are observed. The corresponding emission spectra can be found in Fig. S6–S10†. In addition, dropping a small quantity of diethyl ether to ground samples, the obviously blue-shifted emission colour can be immediately observed, which is less reported for PCL materials, allowing a fast approach to erasing the changed colour. In addition to solvent-fuming, for PCL materials, their luminescent colours of ground samples can be also reversibly switched to original ones by other environmental stimulus, such as heating.[18] With this consideration in mind, the emission colour changes during grinding-heating processes were studied. Heating the ground samples at appropriate temperatures that are determined by the DSC data (*vide infra*), the emission colour of corresponding ground samples have obvious colour changes from orange-emitting to yellow-greenish emitting in different degrees (see Fig. 3). Thus, the heating can also trigger the reversible colour and emission changes. Based on the above results, it can be concluded that alkyl chains play a functional role in turning the molecular packing in solid states as well as PCL reversibility induced by heating and/or solvent fuming. Thereby, the effective iridium(III)-based PCL materials can be constructed through introducing advisable alky chain length into cyclometalated ligand.

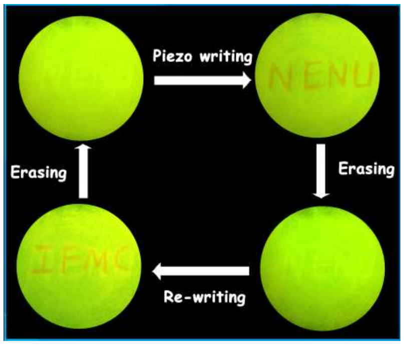


Fig. 4 Photos of the reversible writing/erasing cycle using complex **5** as medium.

Reversible change in emission colour is an important feature for PCL materials to be applied in the real-word applications. Therefore, the reversibility of the mechanochromic processes of complex **5** was investigated as an example. As shown in Fig. S11†, **5** shows good and stable reversibility for both grinding-heating and grinding-fuming cycles. To primarily test the potential applications of PCL iridium(III) complexes in optical device, complex **5** was chosen as a medium due to its relatively remarkable PCL behaviour and excellent reversibility. As shown in Fig. 4, when the as-prepared powder **5** is carefully smeared on a filter paper as a thin film and then solvent fuming, it emits obvious yellow-green light upon excitation with a UV lamp. The word "NENU" was written on this film using a spatula, a clear orange-emitting 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, a reversible colour-change media based on PCL-active iridium(III) complex has been demonstrated, indicating that they are potential to be used 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 numerical data are enumerated in Table 1. It is clearly to show that the exited-state lifetimes (τ) for as-synthesized sample are significantly different to those of ground samples: the grinding results in the evident decease of τ. However, in the case of cationic iridium(III) complex without PCL behaviour, the lifetimes of as-synthesized and ground sample are almost identical. This phenomenon announce that the as-synthesized and ground samples of one same complex exhibit different time-resolved emission-decay behaviours, of which the fundamental cause is altering the mode of solid-state molecular packing and/or the intermolecular interactions after grinding. The ^{1}H NMR spectra of them in different states have been tested as well. Almost no changes were found for these spectra in different states, further validating that the emission colour changes of them should cause by physical processes during the grinding instead of the chemical reaction.

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

The PCL behaviours for organic materials are usually related to the changes of the molecular aggregation morphology such as the packing mode of crystal molecules or the phase transition between crystalline and amorphous states. To gain an insight into the PCL mechanism of the studied iridium(III) complexes, namely complexes **1**–**5**, the powder X-ray diffraction (PXRD) for as-synthesized and ground samples were measured. As can be seen from Fig. 5, all as-synthesized samples show sharp and relatively intense PXRD reflection, indicating that these original powders obtained after column chromatography are well-ordered crystalline structures.[19] In contrast, grinding the as-synthesized samples leads to a broadening and lowering of the intensity of reflection in PXRD patterns, suggesting that the amorphous states formed instead of the ordered structures.[20] After heating or solvent fuming on the ground samples, some sharp diffraction and peaks appeared again (Fig. 5 and Fig. S12–S14, ESI†). Although the heated and solvent-fumed samples of complex **1** shows different reflection peaks with those of as-synthesized sample, it is certain to say that the crystalline structures has formed upon heating or fuming. Thus, it suggests that heating or solvent fuming can convert amorphous ground samples to the crystalline states through molecular repacking and the reversible interconversion of piezochromic luminescence can thus be achieved.

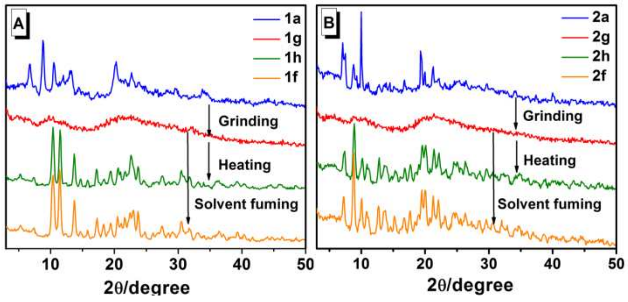


Fig. 5 PXRD patterns of as-synthesized samples and corresponding ground samples.

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. As shown in Fig. 6, there are no endo- and/or exothermic peaks to be detected before their isotropic metal transition for the as-synthesized samples. However, each ground sample exhibits the respective cold-crystallization transition. 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, combing the PXRD and DSC results, it is suggested that the ground samples investigated here are metastable amorphous states. If the ground samples are heated above their recrystallization temperatures or solvent-fuming, they will restore to thermodynamically stable crystals through the recrystallization process. Noticeably, **5g** with long alkyl chains exhibits lower recrystallization temperatures compared with those of **1g**–**4g,** which may be attributed 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. It is possible that long alkyl chains are unfavourable for molecular close packing and endow the materials with low melting points and thermal transition temperature. These findings are similar to recently reported PCL materials based on organic small molecules. Thereby, adjusting the *N*-alky length on cationic iridium(III) complexes can not only design excellent PCL materials but also control their heat-recovering temperature.

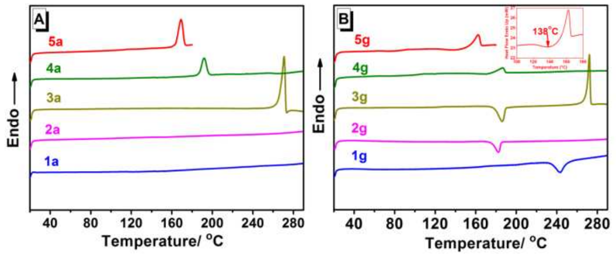


Fig.6 DSC curves of as-synthesized samples (A) and ground samples (B).

Conclusions

In summary, we have designed and successfully synthesized a new class of cationic iridium(III) complexes with the different *N*-alky chains in 2-phenyl-1*H*-benzoimidazole type main ligands. They show strong orange emissions with identical emission profiles in solutions as well as excited-states properties which are well characterized by spectroscopic techniques and theoretical calculations. Interestingly, upon grinding the solid powders, all complexes show naked-eye visible PCL behaviours: their emissions can be repeatedly switched between green and yellow-orange colours by quick grinding–fuming or grinding–heating processes. Moreover, the lengths of *N*-alky chains can effectively adjust their PCL behaviour and thermodynamics properties. The iridium(III) complex with longer *N*-alky chain show larger grinding-induced spectral shifts, leading to more effective iridium(III)-based PCL material. In light of PXRD and DSC data, the interconversion between crystalline and amorphous states upon external stimuli is responsible for the present piezochromism. The relationships between structure and PCL behaviour obtained here will useful to develop and design more promising iridium(III)-based piezochromic materials in future.

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† Electronic Supplementary Information (ESI) available: [Computational details, synthesis and characterisation of complexes **1**-**3**, and corresponding photophysical results]. See DOI: 10.1039/c000000x/

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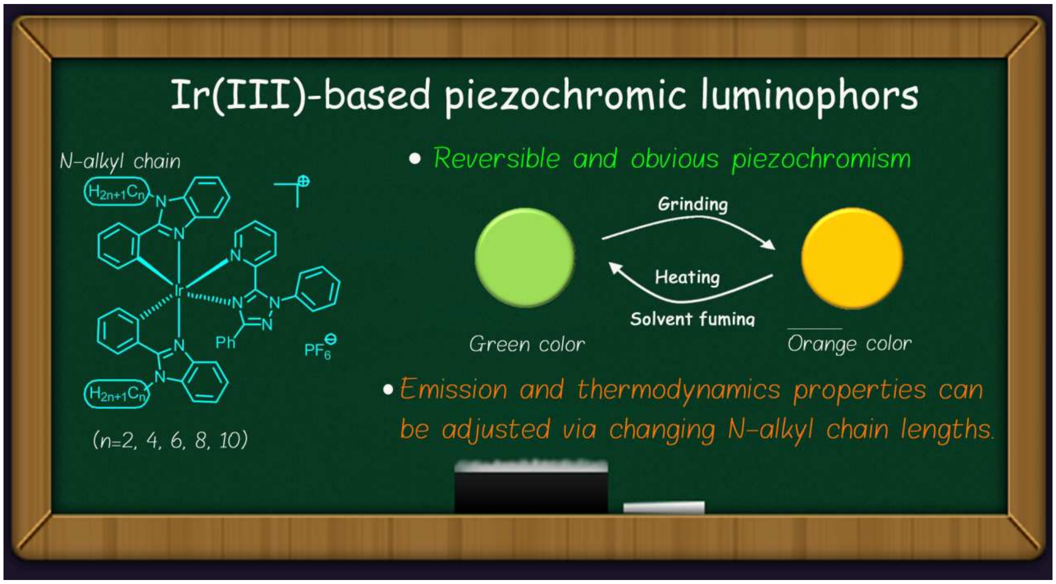

The effect of *N*-alkyl chain lengths on the piezochromic luminescence (PCL) behavior of the Ir(III)-based phosphors is studied. The reproducible and reversible two-colour emission writing/erasing process is achieved by employing the designed Ir(III) materials as a medium.