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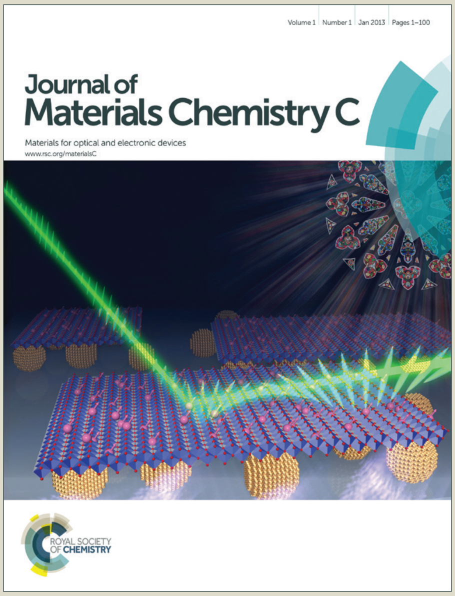

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PAPER

Simultaneous modification of the *N*-alkyl chains on cyclometalated and ancillary ligands of cationic iridium(III) complexes towards efficient piezochromic luminescence properties

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In this study, we have designed and synthesized a series of multifunctional cationic iridium(III) complexes with different lengths of *N*-alkyl chains on 2-phenyl-1*H*-benzoimidazole-based cyclometalated ligands and phenyl-pyridine type ancillary ligands. The photophysical property of each complex has been investigated in details and also ascertained by the comprehensive density functional theory calculations. Unlike negligible influence on their emission spectra and excited-state characteristics in solution, altering the *N*-alkyl chain lengths can efficiently modify their photophysical properties in the solid state. All complexes exhibit fascinating visible piezochromic luminescent (PCL) behaviours. Most interestingly, these iridium(III)-based luminophours with longer *N*-alkyl chains display significant emission colour change and unique reversible feature by mechanical grinding and solvent fuming. The powder X-ray diffraction (PXRD), ^{1}H NMR and MALDI-TOF/TOF mass spectrometer data demonstrate that the phase transitions between crystalline and amorphous states are crucial to the present piezochromism. Moreover, with the merit of high quantum efficiency in aggregate states, the studied iridium(III) complex can serve as an efficient sensor for the sensitive and selective detection of explosive, 2,4,6-trinitrophenol (TNP).

Introduction

Stimuli-responsive luminescent materials presenting colour changes under external stimuli such as heat, light, electricity, pH and mechanical force, are considered as "smart" materials.[1] Such materials have attracted extensive attention due to their academic importance and promising applications.[2] Among them, piezochromic luminescent (PCL) materials showing dynamically optical switch properties to mechanical stimulus or environments possess potential applications in the field of optoelectronics, such as optical recordings, sensors, memories and switches.[3] A commonly pursued approach for changing their emission characteristics is to control the molecular stacking between stable crystalline states and the metastable amorphous states without chemical reaction.[4] Recently, a number of materials displaying PCL behavior have been reported, including organic and inorganic complexes, liquid crystals, polymers as well as metal-organic frameworks.[5] Nevertheless, organometallic complexes with PCL behaviour are rarely reported, although they exhibit preferable photophysical properties. Moreover, the lack of adequate reports on their structure–property relationships brought the difficulty to controllable design and synthesis of PCL materials. Therefore, it is still an enormous challenge to develop new series of organometallic complexes with excellent PCL feature.

Organometallic iridium(III) complexes have arouse wide concern owing to their excellent photophysical and photochemical properties, i.e., high quantum efficiency, as well as tunable emission wavelengths.[6] In recent years, Huang *et al.*,[7] Talarico *et al.*,[8] and our group[9] have developed a set of iridium(III) complexes with intriguing PCL behaviour. The iridium(III)-based rewritable data records and storage devices have been achieved, which will open up a new avenue for the development of multifunctional iridium(III) complexes in the future.[7] Most recently, introducing different alkyl groups on PCL materials have been proven to effectively construct novel PCL dyes and investigate the relationship between the molecule structures and PCL behaviours.[4b, 10] Taking these into consideration, we have designed and synthesized two series of iridium(III) complexes with different *N*-alkyl chain on cyclometalated or ancillary ligands, respectively.[11] The results demonstrate that such chromophores exhibit the opposite PCL effect. For example, the complexes with shorter *N*-alkyl chain on the ancillary ligand display more significant PCL feature but more awkward repeatability. Nevertheless, the ones containing shorter *N*-alkyl chains on the cyclometalated ligand show insignificant PCL properties but better reversibility. It is generally known that both significant PCL feature and repeatability are highly required for the real-world practical applications. Therefore, development of new iridium(III)-based

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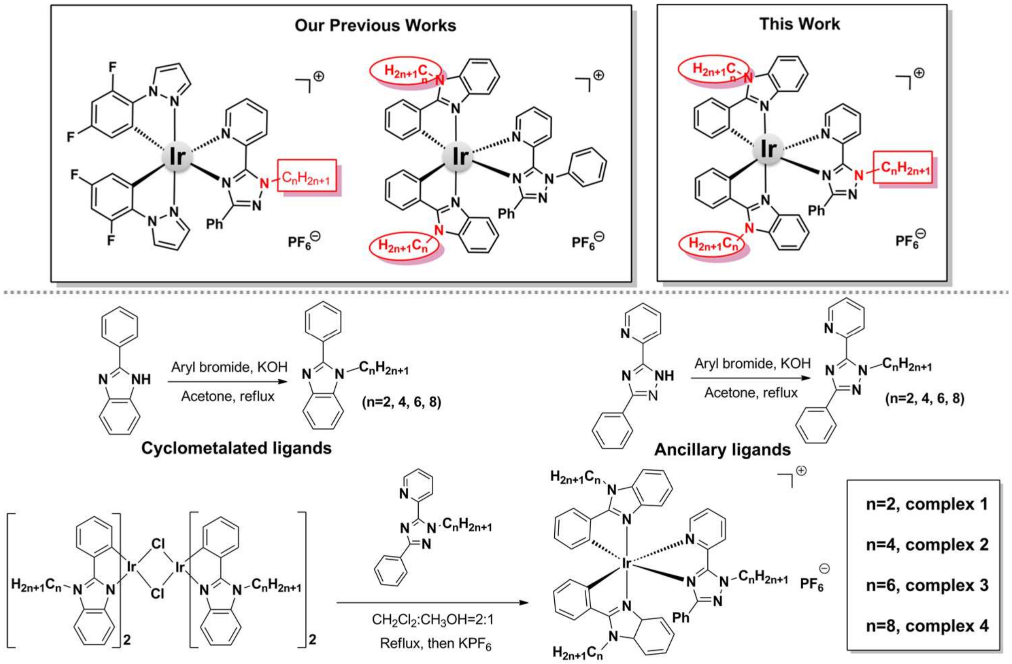

Scheme 1 Chemical structures of the reported Ir(III)-based phosphors and synthesis of the ligands and the iridium(III) complexes studied in this work.

phosphors with efficient PCL behaviour and excellent reversibility is strikingly desirable. Based on our previous works, we speculate that whether such materials can be constructed by simultaneously modifying both ligands of iridium(III) complexes with N-alkyl chains?

Keeping this in mind, we herein report the design and synthesis of a series of iridium(III) complexes with same N-alkyl chains on cyclometalated and ancillary ligands, as shown in Scheme 1. All complexes exhibit obvious piezochromism with the chain length-dependency. More importantly, complex **4** with the longest N-alkyl chain lengths simultaneously showed the most significant PCL property and reversibility with comparison of others. Upon fuming by organic solvent, its emission colour can recover to the original one and this process can be reiterated several times without any deterioration. The obtained results clearly demonstrate that the present mechanochromic behaviour is attributed to the crystal-to-amorphisation phase transformation. Additionally, all synthesized complexes are efficient luminophors in their solid states. With the merits of the high luminescence efficiency, complex **4** can also be used as an effective chemsensor for sensitive and selective detection of nitroaromatic explosives on the ppm scale.

Experimental section

General information and materials

All reagents and solvents employed were commercially available and used as received without further purification. Solvents for syntheses were freshly distilled over appropriate drying reagents. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. NMR spectra were measured on Bruker Avance 500 MHz (^{1}H: 500 MHz, ^{19}F: 470 MHz). The molecular weights of complexes were tested by using electrospray-ionization mass spectroscopy (MS) and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry, respectively. The emission spectra were recorded by 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. Powder X-ray diffraction (PXRD) patterns of the samples were collected on a Rigaku Dmax 2000.

Synthesis

Synthesis of the cyclometalated and ancillary ligands

Scheme 1 depicts the synthetic routes of the cyclometalated and ancillary ligands. As shown in Scheme 1, the ligands used in this work can be easily synthesized by condensation of 2-phenyl-1*H*-benzo[d]imidazole or 2-phenyl-1*H*-benzo[d]imidazole with corresponding aryl bromide in acetone solvent with presence of KOH.[9b, 11b]

Synthesis of the ancillary ligands

2-(1-ethyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Ethtaz)

The precursor 2-(3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (1.11 g, 5.00 mmol) synthesized by a previously reported procedure.[11a, 12] Under nitrogen atmosphere, the precursor was dissolved in acetone. Add the equivalent KOH and stir the mixture for 30 min. Then, bromoethane (0.65 g, 6.00 mmol) was added into the reaction mixture and the mixture was heated to reflux for the overnight. After cooling to room temperature, the mixture was quenched by ice water and then extracted by dichloromethane. The organic layer was dried with Na_2SO_4 and removed the solvent. The obtained residues was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (v:v = 1:2) as the eluent to yield a light-yellow oil (60%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.64–8.65 (m, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.17–8.19 (m, 2H), 7.79–7.81 (m, 1H), 7.44–7.46 (m, 2H), 7.38–7.40 (m, 1H), 7.28–7.30 (m, 1H), 4.87 (t, *J* = 8.0 Hz, 2H), 1.52–1.55 (m, 3H). The related ancillary ligands (Buttaz, Hextaz, and Octtaz) were prepared using the similar procedures.

2-(1-butyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Buttaz)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.66–8.67 (m, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.16–8.18 (m, 2H), 7.81–7.84 (m, 1H), 7.43–7.46 (m, 2H), 7.37–7.40 (m, 1H), 7.31–7.34 (m, 1H), 4.85 (t, *J* = 7.5 Hz, 2H), 1.90–1.96 (m, 2H), 1.37–1.42 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).

2-(1-hexyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Hextaz)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.66–8.67 (m, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.16–8.18 (m, 2H), 7.81–7.84 (m, 1H), 7.43–7.46 (m, 2H), 7.37–7.40 (m, 1H), 7.31–7.34 (m, 1H), 4.83 (t, *J* = 7.5 Hz, 2H), 1.92–1.96 (m, 2H), 1.25–1.38 (m, 6H), 0.86 (t, *J* = 7.5 Hz, 3H).

2-(1-octyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)pyridine (Octtaz)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.66–8.67 (m, 1H), 8.31 (d, *J* = 8 Hz, 1H), 8.16–8.18 (m, 2H), 7.81–7.85 (m, 1H), 7.43–7.46 (m, 2H), 7.37–7.40 (m, 1H), 7.31–7.34 (m, 1H), 4.83 (t, *J* = 7.5 Hz, 2H), 1.92–1.96 (m, 2H), 1.22–1.37 (m, 10H), 0.86 (t, *J* = 7.5 Hz, 3H).

Synthesis of the cyclometalated ligands

Ethyl-2-phenyl-1*H*-benzo[d]imidazole (Eebd)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84–7.86 (m, 1H), 7.73–7.74 (m, 2H), 7.52–7.54 (m, 3H), 7.43 (t, *J* = 4.5 Hz, 1H), 7.31–7.33 (m, 2H), 4.26–4.29 (m, 2H), 1.45 (t, *J* = 7 Hz, 3H).

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

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84–7.86 (m, 1H), 7.72–7.74 (m, 2H), 7.52–7.54 (m, 3H), 7.42 (t, *J* = 4.5 Hz, 1H), 7.31–7.33 (m, 2H), 4.21 (t, *J* = 7.5 Hz, 2H), 1.79 (t, *J* = 7.5 Hz, 2H), 1.25–1.29 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H).

Hexyl-2-phenyl-1*H*-benzo[d]imidazole (Hebd)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84–7.86 (m, 1H), 7.71–7.73 (m, 2H), 7.51–7.54 (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), 1.21–1.25 (m, 6H), 0.84 (t, *J* = 6.5 Hz, 3H).

Octyl-2-phenyl-1*H*-benzo[d]imidazole (Oebd)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.84–7.86 (m, 1H), 7.71–7.72 (m, 2H), 7.50–7.52 (m, 3H), 7.41 (t, *J* = 3.0 Hz, 1H), 7.30–7.32 (m, 2H), 4.20 (t, *J* = 7.5 Hz, 2H), 1.79 (t, *J* = 7 Hz, 2H), 1.19–1.26 (m, 10H), 0.84 (t, *J* = 6.5 Hz, 3H).

Synthesis of the chloro-bridged dimer

The organometallated dimer $[Ir(Eebd)_2Cl]_2$ was synthesized from reaction of $IrCl_3{\cdot}3H_2O$ (0.51 g, 1.43 mmol) with Ethyl-2-phenyl-1*H*-benzo[d]imidazole (Eebd 0.66 g, 3.15 mmol) in 2-ethoxyethanol and water mixture (v:v = 3:1, 32 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: 74%). Other chloride-bridged complexes, $[Ir(Bebd)_2Cl]_2$, $[Ir(Hebd)_2Cl]_2$, $[Ir(Oebd)_2Cl]_2$, was synthesized using a method similar to that for $[Ir(Eebd)_2Cl]_2$. The chloro-bridged dimers were used in the subsequent reactions without further purification.

Synthesis of the complexes

Synthesis and characterization of complex 1

A solution of ligand Ethtaz (0.21 g, 0.63 mmol) and the chloro-bridged dimer $[Ir(Eebd)_2Cl]_2$ (0.56 g, 0.30 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 (v:v = 5:1) and the resulting powders were recrysatallized 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 8.60 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72–7.79 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.29–7.32 (m, 2H), 7.18–7.21 (m, 1H), 7.12–7.14 (m, 3H), 7.05–7.08 (m, 1H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.83–6.86 (m, 2H), 6.76–6.79 (m, 2H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.60 (t, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 5.94 (d, *J* = 7.5 Hz , 1H), 5.68 (d, *J* = 8.0 Hz, 1H), 4.77–4.95 (m, 4H), 4.65–4.68 (m, 1H), 4.55–4.58 (m, 1H), 1.51 (t, *J* = 7.5 Hz, 3H), 1.22–1.31 (m, 6H). ^{19}F NMR (470 MHz, d_6-DMSO, ppm): –67.35 (d, *J* = 711.11 Hz, 6F). MS (MALDI-TOF): m/z 885.3 ($M–PF_6$).

Synthesis and characterization of complex 2

Light-yellow solid, (yield 62%). ^{1}H NMR (500 MHz, d_6-DMSO, ppm): δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.74–7.79 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.24–7.30 (m, 2H), 7.13–7.19 (m, 4H), 7.05–7.08 (m, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.86–6.88 (m, 3H), 6.74–6.75 (m, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 5.99 (d, *J* = 7.5 Hz, 1H), 5.64 (d, *J* = 8.0 Hz, 1H), 4.88–4.97 (m, 3H), 4.51–4.73 (m, 3H), 1.92 (t, *J* = 7.5 Hz, 2H), 1.19–1.69 (m, 10H) , 0.68–0.93 (m, 6H) , 0.66–0.68 (m, 3H) , 1.19–1.69 (m, H). ^{19}F NMR (470 MHz, d_6-DMSO, ppm): –67.35 (d, *J* = 711.11 Hz, 6F). MS (MALDI-TOF): m/z 969.4 ($M–PF_6$).

Synthesis and characterization of complex 3

Light-green solid, (yield 69%). ^{1}H NMR (500 MHz, d_6-DMSO, ppm): δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.34 (t, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.89 (t, *J* = 8.5 Hz, 1H), 7.73–7.79 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.23–7.28 (m, 2H), 7.12–7.17 (m, 4H), 7.04–7.08 (m, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.84–6.89 (m, 3H), 6.69–6.74 (m, 2H), 6.59 (t, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 7.5 Hz, 1H), 6.00 (d, *J* = 7.5 Hz, 1H), 5.64 (d, *J* = 8.0 Hz, 1H), 4.87–4.99 (m, 3H), 4.51–4.69 (m, 3H), 1.91–1.97 (m, 2H), 1.50–1.70 (m, 4H), 0.97–1.39 (m, 17H), 0.75–0.86 (m, 10H). ^{19}F NMR (470 MHz, d_6-DMSO, ppm): –67.35 (d, *J* = 711.11 Hz, 6F). MS (MALDI-TOF): m/z 1053.5 ($M–PF_6$).

Synthesis and characterization of complex 4

Light-green solid, (yield 74%). ^{1}H NMR (500 MHz, d_6-DMSO, ppm): δ 8.63 (d, *J* = 7.5 Hz, 1H), 8.34 (t, *J* = 7.5 Hz, 1H), 7.95–7.99 (m, 2H), 7.89–7.91 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.22–7.28 (m, 2H), 7.12–7.19 (m, 4H), 7.04–7.07 (m, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.83–6.89 (m, 3H), 6.74 (t, J = 7.5 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 6.16 (d, J = 7.0 Hz, 1H), 6.00 (d, J = 7.5 Hz, 1H), 5.62 (d, J = 8.0 Hz, 1H), 4.90–5.00 (m, 3H), 4.51–4.68 (m, 3H), 1.92–1.95 (m, 2H), 1.49–1.70 (m, 4H), 0.97–1.37 (m, 29H), 0.69–0.87 (m, 10H). ^{19}F NMR (470 MHz, d$_6$-DMSO, ppm): –67.35 (d, J = 711.11 Hz, 6F). MS (MALDI-TOF): m/z 1137.6 (M–PF$_6$).

Theoretical calculations

All calculations on the ground and excited electronic states of the complexes were carried out at the PBE0 level within the Gaussian 09 software package[13] together with 6-31G* basis sets for C, H, N atoms and the LANL2DZ 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 lowest-lying triplet (T$_1$) states were fully optimized and calculated at the spin-unrestricted UPBE0 level with a spin multiplicity of 3. All expectation values calculated for S^2 were smaller than 2.05.

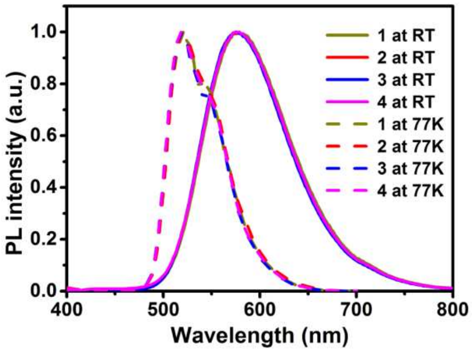

Fig. 1 Emission spectra of complexes **1–4** in CH$_3$CN (1×10^{-5} M) at 298 and 77 K.

Results and discussion

Photophysical properties in solution and solid state

Fig.1 shows the emission spectra of complexes **1–4** in CH$_3$CN solution at room temperature (RT) and 77 K, the relevant data are summarized in Table S1†. The sub-microsecond ranges of emissive lifetimes clearly demonstrate the phosphorescent emission nature of them.[14] It is well known that three excited states can contribute to the observation of light emission for cationic iridium(III) complexes, named spin-forbidden metal-to-ligand charge transfer (^{3}MLCT) and ligand-to-ligand charge transfer (^{3}LLCT) and ligand-centered (LC$^3\pi$-π*) characters.[15] As shown in Fig. 1, at room temperature, complexes **1–4** exhibit the broad and featureless emission spectra in solution, indicating that the emissions of them mainly originated from ^{3}MLCT and/or ^{3}LLCT states other than LC $^3\pi$-π*, since the emissions from LC $^3\pi$-π* states always are vibronically structured.[6c] After cooling the solution to 77 K, all complexes display largely blue-shifted emissions spectra compared with those at RT. (Fig. 1). It is noteworthy that although the different alkyl chains are attached into these complexes, they display a similar emission pattern at RT and 77 K. These results suggest that altering the N-alkyl chains on both ligands shows negligible impact on their phosphorescence spectra as well as excited-state characteristics in solution. To verify this issue, the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations on them have been performed to ascertain the nature of their excited states. As depicted in Fig. 2, the highest-occupied molecular orbital (HOMO) of complex **1** mainly resides on the benzimidazole group of the cyclometalated ligands and the iridium ion, while the lowest unoccupied molecular orbital (LUMO) primarily delocalizes over the pyridine and 1,2,4-triazol moieties of the ancillary ligands. Complexes **2–4** show almost identical HOMO and LUMO distributions (see Fig. S1, ESI†). Clearly, the *N*-alkyl chains in **1–4** do not contribute to neither the HOMOs nor LUMOs. The TD-DFT data show that the lowest-lying triplet (T$_1$) states of the complexes mainly originate from the excitation of HOMO→LUMO (see Table S2, ESI†). Therefore, the T$_1$ states have predominantly mixed ^{3}MLCT and ^{3}LLCT characteristics. The charge transfer nature of the emitting triplets is in agreement with the experimental emission spectra. In addition, the unpaired-electron spin density distribution perfectly matches the topology of the HOMO→LUMO excitation from which the T$_1$ excited-states originate (see Fig. 2). These results further confirm that the mixed ^{3}MLCT and ^{3}LLCT excited-state characters are attributed to the T$_1$ states of them and the different *N*-alkyl chains have little effect on their emission in solutions.

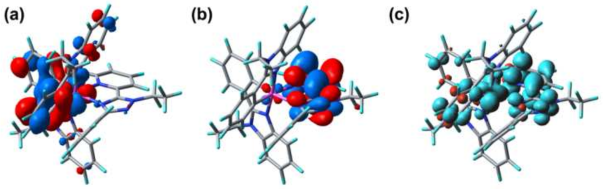

Fig. 2 Electronic density contours calculated for the HOMO (a) and the LUMO (b) of complex **1**. (c) Spin density distribution calculated for complex **1** in the T$_1$ excited state.

Table 1 Emission maxima (λ, in nm) of as-synthesized, ground and fumed complexes **1–4**.

complex	$\lambda_{as\text{-}synthesized}$	λ_{ground}	$\Delta\lambda_{PCL}$[a]	λ_{fumed}
1	542	563	21	548
2	536	559	23	553
3	513	550	37	544
4	519	552	33	520

[a] $\Delta\lambda_{PCL} = \lambda_{ground} - \lambda_{as\text{-}synthesized}$

Despite **1–4** exhibit identical emission spectra as well as luminescent colour in solutions, their solid-state emissions are obviously different. They display bright luminescence with emission colour ranging from yellow (542 nm for **1**) to green (513 nm for **4**), respectively. The relevant solid-state emission data are given in Table **1**. It is generally recognized that the solid-state emission properties of luminophors strongly depend on the molecular arrangement motif and intermolecular interactions.[16] As a result, we conjecture that adjusting *N*-alkyl chains attached at iridium(III) complexes can induce different molecular packing and hence emission colour in solid-states. The longer *N*-alkyl chains might impede the close packing, which results in the loose molecular packing and blue-shifted emission spectra. Similar to pervious reports, simultaneously modifying the *N*-alkyl chain on both ligands of cationic iridium(III) complexes is also an effective approach to control their photophysical properties in the solid state.[11]

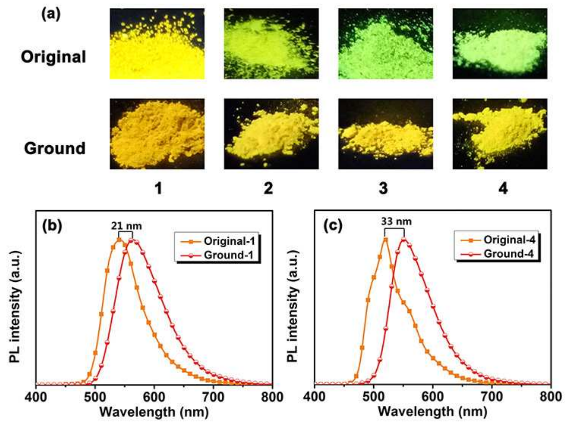

Fig. 3 (a) Photographs of complexes **1**–**4** taken under UV illumination (365 nm). Emission spectra of complexes **1** (b) and **4** (c) in the solid states at room temperature, respectively.

Solid-state piezochromic properties

Organic solid-state materials with tunable light-emitting behaviours have attracted much attention due to their potential applications as sensors, logicgate units, memories, etc.[17] Developing such efficient materials and deeply investigating the relationship between the structure and the PCL behaviour will be valuable for further molecular design. In our previous work, the effect of *N*-alkyl chains on PCL properties was successfully accomplished, in which the *N*-alkyl chains were grafted on either cyclometalated or ancillary ligands.[11] To evaluate the PCL behaviours of iridium(III) complexes studied in this work, their solid-state emissions were investigated. As shown in Fig. 3a and Table 1, the as-synthesized solid powder of complexes **1**–**4** emit intense yellow or green light at 542, 536, 513 and 519 nm, respectively. After grinding of the original powders in agate mortars with pestle, the noticeable colour change in the luminescence are observed (see Fig. 3a). Meanwhile, as visualized by the naked eyes, it is found that the complexes with longer *N*-alkyl chains show more remarkable colour changes in comparison with those of the shorter ones. In other words, the grinding induced spectral shift ($\boldsymbol{\Delta}\lambda_{\mathrm{PCL}}$, $\boldsymbol{\Delta}\lambda_{\mathrm{PCL}} = \lambda_{\mathrm{ground}} - \lambda_{\mathrm{as\text{-}synthesized}}$) of these iridium(III) luminophors are length-dependent, which is similar to recently reported works. Herein, we take **1** and **4** as examples. The emission spectra of **1** and **4** in original and ground states were studied and shown in Fig. 3b and Fig. 3c. It is clear that the grinding result in the broadened emission spectra, showing obvious emission wavelength changes of 21 nm for **1** and 33 nm for **4**, respectively. It is generally recognized the PCL behavior for a given luminophor is related to the arrangement of its molecular motifs as well as the intermolecular interactions. Usually, the PCL materials with weak intermolecular interactions, especially the materials functionalized with different alkyl chains, exhibit more significant PCL properties than those with strong ones.[10b, 10c] Moreover, the existence of a large dipole moment for a D-π-A PCL dyes is also favorable to the significant PCL behaviors.[3f] In this work, however, there are no D-π-A structures in the studied system. Thereby, it is speculated that introducing long alkyl chains on both cyclometalated and ancillary ligands can weaken the intermolecular interactions more effectively. As a result, the grinding may result in more significant PCL feature for iridium(III) complexes with longer alkyl chains.

As mentioned above, the cationic iridium(III) complexes possessing longer *N*-alkyl chains exhibit more efficient PCL behaviour with lager emission wavelength changes. However, whether it can also exhibit excellent colour-change reversibility that triggered by external stimuli, such as grinding-solvent fuming. To check their reversibility, the grinding-fuming switching experiment was performed. All ground samples can be stable for months at room temperature. Treating the ground samples with ether solvent, however, the emissions are obviously blue-shifted in different degrees compared to those of ground ones (see Fig. 4, Fig. S2 and Fig. S3†). It is worth mentioning that only complex **4** exhibits more excellent reversibility, whose emission of ground sample can perfectly revert to the original one with the same spectra profile and emission maximum (Fig. S2 and Fig. S3†). Further grinding the fumed sample **4** again leads to the orange-emitting form as seen in Fig. 4a. Its emissions can thus be reversibly switched between green-emitting and orange-emitting states for several times by the grinding-fuming cycles with almost no fatigue. Nevertheless, the solvent-fuming cannot entirely induce emission colour of ground samples **1**–**3** to their original ones. For instance, the emission colour of fumed-**2** was nearly invariant with only 6 nm spectral shift with respect of its ground sample. Simultaneously attaching the long *N*-alkyl chains on ligands of cationic iridium(III) complexes may more effectively decrease the intermolecular interactions, which endows them with a large colour-switchable feature as well as good reversibly. Thereby, it is believed that introducing advisable alkyl chains into cationic iridium(III) complexes to control their molecular packing is a feasible way to design and construct effective iridium(III)-based PCL materials.

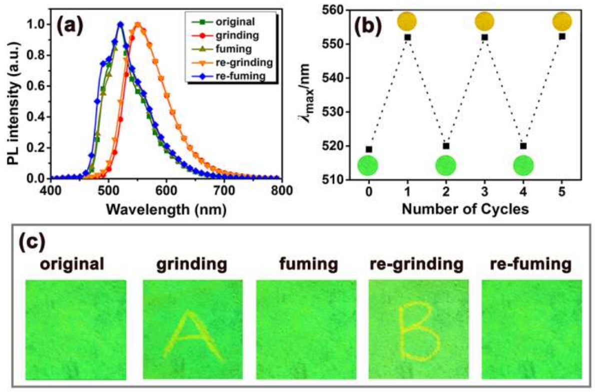

Fig. 4 (a) Emission spectra of complex **4** in various states at room temperature. (b) Maximum emission wavelength change *versus* repeating cycles. (c) Photographs of the reversible writing/erasing cycle using complex **4** as medium.

It is envisioned that complex **4** can be used as an appropriate optical memory device by judicious utilization of its mechanochromism. To demonstrate its useful practical application, a small quantity of solid powders **4** was carefully spread on a filter paper as thin film and then subjected to solvent fuming (Fig. 4c). The strong green-emitting film is observed under 365 nm UV irradiation. The letter of "A" was written on the film using a metal spatula, and a clear orange-emitting pattern "A" with large colour contrast appears, which can be readily distinguished from the bright green background. Then, fuming the film with diethyl ether or dropping a spot of diethyl ether on the film, the letter "A" is immediately erased by converting the luminescent colour back to the background emission. Then, a new word "B" with orange-emitting colour can be re-written on this film and erased using the same method as mentioned above, demonstrating a reproducible recording-erasing process. Such fascinating features make complex **4** a promising material for recyclable optical recording and security inks.

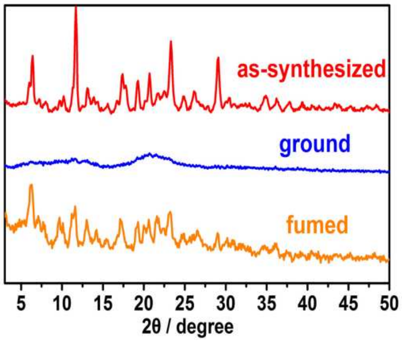

Fig. 5 PXRD patterns of complex **4** in various states.

The mechanism for the present piezochromic behaviour

Since the solid-state emission of luminophors strongly depend on the molecular structure as well as the solid packing, alteration of molecular arrangement motif or phase transition between crystalline and amorphous states in response to pressure, was commonly considered as the main reason of their piezochromic luminescent properties. To gain more insight into the PCL mechanism of these iridium(III) complexes, the powder X-ray diffraction (PXRD) analysis was carried out, as shown in Fig. 5 and Fig S4†. Taking complex **4** as a representative example, the as-synthesized powder shows many sharp and intense diffraction peaks, which suggests that the solid powders obtained by column chromatography are well-ordered crystalline structures.[18] In contrast, after grinding, the XRD profile shows only a few broad and weak signals, which are indicative of the transition from a crystalline to an amorphous phase.[19] Similar observations are also found in other complexes (see Fig. S4†). After careful treatment of the ground samples of complex **4** with drops of diethyl ether or long time solvent-fuming, the clear reflection peaks appear again, which well fit those of original as-prepared solid sample, demonstrating reversion from the amorphous to the crystalline phase. Although some fumed solids show different diffraction peaks with those of as-synthesized ones (**1**–**3**), it is also certain to say that the crystalline structures have formed upon fuming. Consequently, the PXRD results indicate that the emission colour changes observed upon grinding are ascribed to the phase transition between crystalline and amorphous states. It is proved that the ground samples are amorphous metastable states, which can recover to the crystalline ones upon external stimulus. Once the amorphized powders are fumed by the solvent, they can spontaneously arrange themselves into a crystalline form. For complex **4**, the longer alkyl chains in it will provide higher molecular mobility in comparison with others. Upon the solvent fuming, the ground sample **4** can effectively recover to the original crystalline powder, which is further confirmed by the similar PXRD profile between the original and the fumed powders. This is a possible reason why complex **4** exhibits the better reversibility than others.

Moreover, the time-resolved emission decay behaviours after and before grinding, the excited-state lifetimes of complexes **1**–**4** in various states were studied. The lifetime data are illustrated in Table S2†. As shown in Table S2, the weighted mean lifetimes <*τ*> of all ground samples are significantly different with those of original ones. The longer lifetime were achieved after grinding. The reported cationic iridium(III) without PCL behaviours, however, show almost identical lifetimes under various conditions. Therefore, it can be concluded that the changes in the emission colour of these iridum(III)-based PCL materials are associated with alteration of the mode of solid-state molecular packing and/or the intermolecular interactions and hence changed their excited-state lifetime. The same ^{1}H NMR spectra of them in various states further confirm this point. The mechanochromic effects presented herein are thus caused by physical processes during the grinding rather than by a chemical reaction.[3a]

Selective detection of 2,4,6-trinitrophenol TNP

Recently, detection of high explosives has become important due to homeland security, environmental and humanitarian implications.[20] Most high explosives are nitro-substituted organic compounds, such as 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT). Among them, TNP exhibits more superior power than the well-known TNT and is widely used in fireworks, dyes and so on, which usually results in the contamination of soil and aquatic systems.[20b, 21] In the purpose of highly sensitive and selective detection of TNP in aqueous media, various chemosensors based on the organic luminescent materials have been developed to date. Nevertheless, the traditional aggregation caused quenching effect in aquatic systems always results in drastically negative effects on the efficiency and sensitivity of the sensors. Recent reports indicate that the efficient luminophors with appropriate emission wavelength can be used as sensitive sensor to detect TNP.[22] Therefore, we herein chose complex **4** to explore its utility as chemosensor for detection of explosive due to its obvious aggregation-induced emission enhancement feature (see Fig. S5).

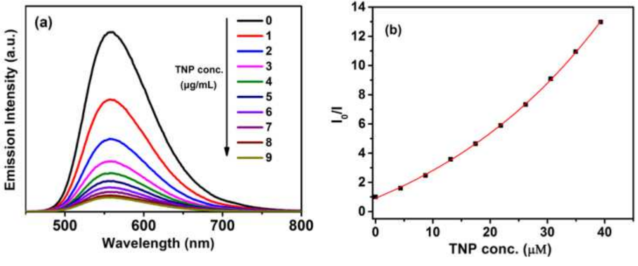

Fig. 6 (a) Photoluminescence spectra of complex **4** in acetonitrile-water (v/v = 1: 9) mixtures containing different amounts of TNP. (b) Corresponding Stern–Volmer plots of TNP.

As shown in Fig. 6a, the nanoaggregates of complex **4** exhibit intense emission in the acetonitrile-water (v:v = 1:9, by volume) mixture. However, a visible emission quenching is observed with addition of a small amount of TNP into the mixtures. The luminescence intensity obviously decreases below 50% at TNP concentration of 2 ppm. When the TNP concentration reached 9 ppm, the negligible emission can be observed with a quenching efficiency of nearly 92%. The Stern–Volmer (SV) curve, as depicted in Fig. 6b, gives curves bending upward, which indicates that the emission quenching becomes more efficient upon adding the TNP concentration. The quenching constant is evaluated to be 1.6×10^{6} M^{-1} by using the SV equation $(I_0/I) = K_{SV}[A] + 1$, where I and I_0 are the emission intensities with and without quencher, respectively, K_{SV} is the quenching constant (m^{-1}), [A] is the molar concentration of the quencher.[23] Such quenching constant is higher than those of the reported fluorescent sensors for explosive detection, demonstrating that **4** shows a high sensitivity to TNP.[24] Moreover, the selectivity is another key factor for a senor. To check the sensing selectivity of complex **4**, the emission quenching experiments for other nitro aromatics, including TNT, 2,4-dinitroluene (2,4-DNT), nitrobenzene (NB), 2,6-dintritoluen (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), 2-Nitrotoluene (oNT) and 3-Nitrotoluene (mNT), were studied. As shown in Fig. 7, each nitroaromatic compound exhibits relatively less effect on emission quenching under the same condition. Evidently, the emissive nanoaggregates of complex **4** perform both high sensitivity and selectivity toward TNP, exploiting the potential applications of the cationic iridium(III) complexes in future. Since the LUMO energy of **4** is higher than those of nitroaromatic analytes, which facilitates the jump of electrons to the lower ones of analytes, leading to photo-induced electron transfer-caused (PET) emission quenching of **4** (see Fig. S6†).[25]

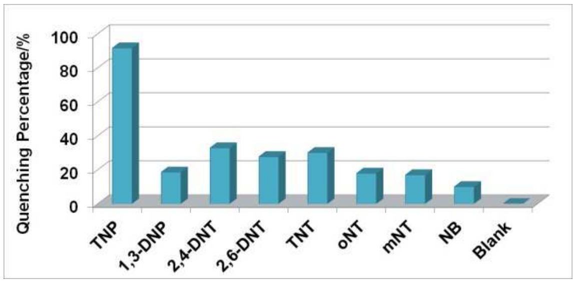

Fig. 7 Quenching percentage obtained for different analytes (9 ppm).

Conclusions

In summary, we have designed and synthesized a series of cationic iridium(III) complexes with similar structures but different *N*-alkyl chains on both ligands. In sharp contrast to the same emission in solution, their solid-state photophysical properties exhibit the *N*-alkyl chain length dependency, showing obviously blue-shifted emission with extending the chain lengths. After grinding, each complex undergoes visible PCL. Among them, complex **4** with the longest chains feature more efficient PCL property with larger grinding-induced emission colour change. More importantly, after treatment of ground powders with organic solvents, the emission colour of ground sample **4** can perfectly revert to its original one, but not to others complexes. A reproducible two-colour emission writing/erasing process for **4** was thus achieved. It is believed that simultaneously introducing an appropriate *N*-alkyl chains into cationic iridium(III) complexes is a feasible design strategy for constructing the effective iridium(III)-based PCL materials with good reversibility. As supported by XRD data, the present piezochromism is attributed to the transformation between crystalline and amorphous states. Inspired by intrinsic characteristics of these phosphors, a highly sensitive and selective TNP sensor based on complex **4** has been also demonstrated. The present study will provide a new insight into the design of multifunctional cationic iridium(III) complexes for optical devices and sensors in the near future.

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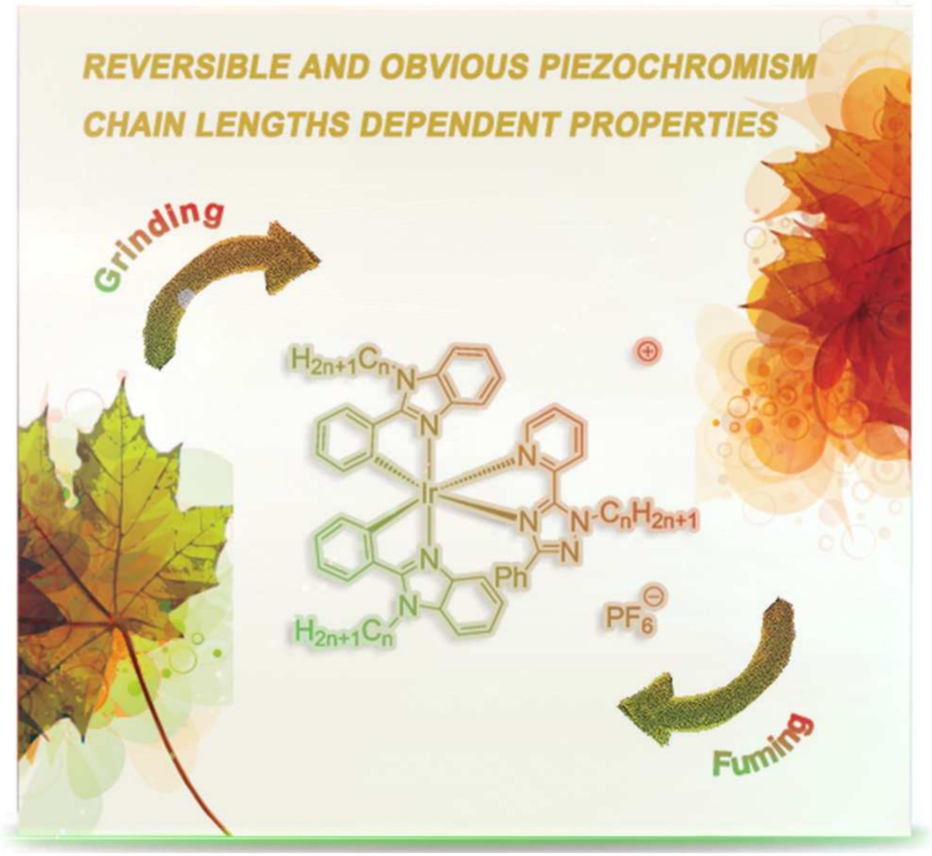

Cationic Ir(III)-based piezochromic luminescence (PCL) materials exhibiting efficient PCL feature as well as excellent reversibility can be achieved by simultaneously modifying both ligands using appropriate N-alkyl chains.