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## COMMUNICATION

## Reversible piezochromic behavior of two new cationic iridium(III) complexes<sup>†</sup>

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We demonstrate that two new cationic Ir(III) complexes exhibit an interesting piezochromism, and their emission color can be smartly switched by grinding and heating. This is the first example that the Ir(III) complexes display piezochromic phosphorescence.

Solid-state organic luminophoric molecules have received tremendous attention due to their potential applications in molecule-based devices.<sup>1</sup> It is also generally recognized that their emission properties strongly depend on the molecular arrangement motif and intermolecular interactions. Accordingly, tuning and switching of luminescence could be realized through external stimulus affecting the mode of molecular packing.<sup>2</sup> Piezochromism,<sup>3</sup> as an interesting phenomenon, has been presented and investigated on the basis of a series of pure organic small-molecules,<sup>4</sup> some metal complexes (Au<sup>I</sup>, Ag<sup>I</sup>, Zn<sup>II</sup>, Pt<sup>II</sup>, Al<sup>III</sup>),<sup>3b,5-9</sup> liquid crystalline materials and polymers<sup>10</sup> recently. As is shown by chemists, difference in the molecular packing motifs allows materials undergo the color change in luminescence upon grinding and subsequently reverts to its original color by heating or recrystallization. This provides an executable strategy to tune the luminescence of compounds and is thought to be of importance for various recording and sensing applications.11

Phosphorescent Ir(III) complexes are of increasing interest because of their outstanding photophysical properties and superior photo- and chemical stability, suggesting that Ir(III)-based complexes have recently emerged as good candidates for various applications including chemical sensors,<sup>12</sup> organic light-emitting diodes (OLEDs),<sup>13</sup> light-emitting cells (LECs)<sup>14</sup> and biological cell imaging.<sup>15</sup> Ir(III) complexes with triazole–pyridine derivatives as ancillary ligands have shown intriguing properties as the outstanding materials for optical devices.<sup>16</sup> Moreover, the desirable blue-emitting Ir(III) could be realized due to the strong  $\sigma$ -donor property of the triazole ring. Recently, a series of cationic Ir(III) complexes with

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(2-(5-methyl-2-phenyl-2*H*-1,2,4-triazol-3-yl)pyridine, Mptz) ancillary ligands have been designed and synthesized in our laboratory. During the investigation of their photophysical properties, we discovered that the complexes underwent remarkable emission color changes upon grinding. This interesting observation prompted us to further study their luminescence behaviors. It is believed that if the Ir(III) complexes are also capable of showing reversible piezochromic property, new opportunities for Ir(III) complexes in optical recording could be well expected.

Here, we report our preliminary investigation on two new cationic iridium complexes with piezochromic property, namely,  $[Ir(dfppz)_2Mptz]PF_6$  (**B1**) and  $[Ir(ppy)_2Mptz]PF_6$  (**Y1**), respectively (Scheme 1). Their emission colors show reversible interconversion from blue to blue-green for **B1** and from green to orange for **Y1**, respectively, upon grinding. To the best of our knowledge, this is the first report on piezochromic phosphorescence of the cationic iridium(III) complexes.

Treatment of organometallated dimer 1-(2,4-difluorophenyl)-1*H*-pyrazole (dfppz) and 2-phenylpyridine (ppy) with corresponding ancillary ligands Mptz by a bridge-splitting reaction in dichloromethane–methanol (2 : 1), then readily give complexes **B1** and **Y1**. Their identities have been characterized spectroscopically, with satisfactory results obtained (Fig. S1–S4, ESI†). The crystals of **B1** were obtained by recrystallization from dichloromethane–ether. X-Ray suitable crystals of **B1** were obtained as prismatic crystals which show high blue emission upon irradiation of UV-light. (Fig. S5, ESI†). The structure of **B1** exhibits a distorted octahedral geometry around the Ir atom coordinated by two cyclometalated ligands and one ancillary ligand. Here, the two dfppz ligands adopt mutually an eclipsed configuration with two nitrogen atoms residing at *trans* locations, and no solvent molecules are found



Scheme 1 Chemical structures of complexes B1 and Y1.

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Fig. 1 Emitting color upon irradiation of UV-light of B1 and G1 (a); and Y1 and O1 (b); (c) and (d) the luminescence spectra of complexes B1, G1, Y1 and O1; (e) and (f) repeated cycles of the piezochromism; B1 (g) and Y1 (h) were cast on the filter paper and the letters "Ir" and "Su" were written with a spatula under UV-light at room temperature.

in the unit cell (Fig. S6, ESI<sup>†</sup>). As seen from the crystalline structure of **B1**, there are weak C–H··· $\pi$  intermolecular interactions and the dimer-like structures are observed in the packing diagram (Fig. S7, ESI<sup>†</sup>). Owing to the weak intermolecular interactions, the molecular packing was relatively loose and the ordered crystal structures might be easily collapsed by external pressure.<sup>4b,e,f,5a</sup> The emission property of **B1** would also be changed as a result of the alteration of solid-state arrangement and/or phase transition.

When the blue-emitting solid state powder **B1** was ground in a ceramic mortar, the obtained light-green powder emits bluegreen luminescence **G1** at 493 nm with respect to 461 nm of **B1** (Fig. 1a). Evidently, **B1** exhibits pressure-induced luminescence change feature, that is, **B1** is a piezochromic material. Similar to that of **B1**, after grinding treatment of **Y1**, the sample unexpectedly converts into **O1** with orange-emitting color (Fig. 1b). Since <sup>1</sup>H NMR, MALDI-TOF spectra and elemental analysis of **B1** (**G1**) and **Y1** (**O1**) gave the same value corresponding to [Ir(dfppz)<sub>2</sub>(Mptz)]PF<sub>6</sub> and [Ir(ppy)<sub>2</sub>Mptz]PF<sub>6</sub> (Fig. S8 and S9, ESI<sup>†</sup>), it indicates that no chemical reaction happens during the grinding process and further implies that different emission properties of them were caused by physical processes, such as changing the intermolecular interactions and/or the mode of the molecular packing (Fig. 1c and d). The blue-green (G1) and orange (O1) luminescence can be easily reverted to blue and green ones upon recrystallizing from a dichloromethane–ether mixture or heating at 230 °C for 10 min (Fig. S10, ESI†). Further grinding of the heated-samples again forms the blue-green- or orange-emitting ones. Noticeably, an additional high-energy peak was observed for the heated sample G1, but its XRD curves and NMR are identical. The potential reason responsible for that is under investigation. However, the color changes in solid state emission can be repeated many times, indicative of an excellent reversibility in the switching processes (Fig. 1e and f), which is similar to the reported piezochromic material based on organic small-molecules.<sup>4e,17</sup>

The solid state samples **B1** and **Y1** were then outspread on the filter paper and the letters "Ir" and "Su" were written on that with a spatula, respectively. The blue-green "Ir" and orange "Su" can be observed clearly on the blue and green "paper" with the naked eye under the UV light (Fig. 1g and h), implying that both of them (**B1** and **Y1**) have potential application as optical recording materials.

To understand the possible origin of the present piezochromic behavior, the powder X-ray diffraction (PXRD) of each sample was studied (Fig. 2a and b). XRD patterns of **B1** are consistent with the single-crystal diffraction data. The intensive and sharp reflection peaks can also be observed in **Y1**, indicating that **B1** and **Y1** should be the well-ordered aggregates. While, the ground samples **G1** and **O1** show very weak and broad diffraction signal intensity, indicating that the amorphous states formed instead of the original ordered structures. After heating or recrystallization on the ground samples, some sharp diffraction peaks appeared (Fig. 2 and Fig. S11, ESI†). It suggests that heating or recrystallization can convert amorphous ground samples to the crystalline states through molecular repacking and the reversible interconversion of piezochromic luminescence can therefore be achieved (Fig. 1e and f).

The thermal properties of all samples obtained from different treatments are carefully analyzed by differential scanning calorimetry (DSC). The DSC curves for the heating of unground sample **B1** and heated **G1** only exhibited an almost identical endothermic peak at 318 °C, corresponding to their melting



**Fig. 2** Power X-ray diffraction pattern (a and b) and the DSC curves (c and d) of the corresponding samples.

points (Fig. 2c). In contrast, upon heating amorphous states G1, their DSC curves firstly exhibit an exothermic recrystallization peak at relatively lower temperatures of about 150 °C, and then an endothermic melting peak was detected, which is similar to the melting points of corresponding crystalline state samples. It is due to the fact that as the temperature increases, the amorphous solid will become less viscous and the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. In addition, because the melting point of Y1 in different states is higher than their decomposition temperature (Fig. S12, ESI<sup>†</sup>), the DSC of Y1, O1 and heated O1 was only recorded from RT to 300 °C. As depicted in Fig. 2d, it is clear that except O1 with a recrystallization peak at about 220 °C, there are no endo- and/ or exothermic peaks prior to 300 °C. The results indicate that the ground samples are in a metastable state which can be restored to thermodynamically stable crystals (B1 and Y1) from the powder (G1 and O1) through an exothermic recrystallization process.

The <sup>13</sup>C magic-angle spinning nuclear magnetic resonance (CP/MAS-NMR) spectroscopy was also used to provide deep insight into the piezochromic behaviors of the B1 and Y1 crystalline powders. As shown in Fig. S13, ESI<sup>†</sup> the ground samples G1 and O1 also keep their original conformation at the molecular level. In crystalline samples, they show clear sharp resonance lines. By contrast, the resonance lines of ground samples exhibit broader distribution compared with those of crystalline ones. Based on our experimental results, we can confidently propose that the ground samples, obtained by the mechanical grinding, are a kind of **B1** and **Y1** amorphous state powders.<sup>18</sup> The <sup>15</sup>N NMR data also support these results (Fig. S14, ESI<sup>+</sup>). Although the intermolecular interaction property of amorphous states cannot be determined accurately at the current stage, the emission properties of these two complexes may be strongly molecular packing dependent. Moreover, the photoluminescence decays of the samples before and after grinding were also performed, revealing that emission lifetimes for crystalline states are longer than those for amorphous ones (Fig. S15, ESI<sup>+</sup>).

In summary, we have successfully prepared and discovered two cationic complexes exhibiting a fascinating piezochromic phosphorescence, in which the emission color can be switched reversibly by grinding and heating. This is the first report that the Ir(III) complexes display piezochromic phosphorescence. Based on the PXRD, DSC and CP/MAS NMR studies, we found that this piezochromic phosphorescence origin could be attributed to a crystalline–amorphous phase transformation. This reversible color change feature will be useful in developing new application for Ir(III) complexes, such as optical recording, temperature- or pressure-sensing in future.

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