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Introduction

Persistent room-temperature phosphorescence (p-RTP) materials have gained increasing attention because of their unusual generation processes and promising practical applications, including biological imaging, chemical sensing, and security protection.¹ However, efficient phosphorescent emission is commonly observed in inert gas atmospheres or at ultra-low temperatures; achieving p-RTP in air and at room temperature is difficult because triplet excitons tend to relax nonradiatively *via* internal or external quenching.² In recent decades, mechanical-force-responsive luminescence materials

Persistent room-temperature phosphorescence or high-contrast phosphorescent mechanochromism: polymorphism-dependent different emission characteristics from a single gold(I) complex[†]

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Luminophores with persistent room-temperature phosphorescence (p-RTP) or effective phosphorescent mechanochromism features have significant potential applications in the field of optoelectronic materials. Until now, p-RTP and remarkable phosphorescent mechanochromism phenomena have been observed in some luminescent molecules with different molecular structures. However, separately realizing p-RTP and high-contrast phosphorescent mechanochromism in different polymorphs from a single luminophore is still a valuable and challenging topic. In this work, two polymorphs **1B** and **1YG** of a new gold(I) complex with blue and yellow-green luminescence, respectively, are reported. Interestingly, **1B** exhibits high-contrast phosphorescent mechanochromic behavior, while **1YG** exhibits a persistent room-temperature phosphorescence effect. This is the first example of simultaneously obtaining double-purpose crystalline materials with a high-contrast phosphorescent mechanochromism or persistent room-temperature phosphorescence feature from a single luminophore.

have triggered significant interest owing to their numerous potential applications, including force sensing and optical recording, and in anti-counterfeiting systems.³ For high-performance mechanochromic materials, two factors are vital: (1) strong solid-state luminescence and (2) high-colour-contrast before and after mechanical stress. At present, a range of mechanochromic fluorophors, which involve fluorescent color changes under mechanical stimulation, have been realized;⁴ however, phosphorescent mechanochromic organic molecules are still scarce.⁵ In general, organometallic complexes are more promising for obtaining phosphorescent mechanochromism in comparison with organic compounds. However, to date, although some metal-organic complexes possessing phosphorescent mechanochromic behavior have been discovered,^{6,7} mechano-responsive metal complexes with longlived RTP features are rather rare.

Gold, as an important transition metal, is proven to be able to display the maximum relativistic effect compared with its neighbouring elements. Over the last two decades, gold(i)chemistry has continued to receive growing attention, and a variety of structurally novel gold(i) complexes with rich photophysical properties have been reported.⁸ Nevertheless, simultaneously achieving p-RTP and high-contrast phosphorescent mechanochromism from a gold(i) complex still remains a challenge.

Polymorphism is considered as an intriguing crystallization phenomenon, in which a single substance can generate two or

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more crystalline phases in different or even the same crystallization environments, and these crystalline phases have distinct molecular arrangements in the crystal lattice.9 It is well known that the physical and chemical characteristics of crystals are closely associated with their crystal structures; thus, different polymorphs resulting from the same substance are likely to exhibit varying photophysical properties. Indeed, obtaining multipurpose crystalline materials from a single luminophore by taking advantage of structural polymorphism is a significant but challenging research topic. Herein, a newly reported gold(I) isocyanide complex 1 is demonstrated, which generated two distinct polymorphic crystals 1B and 1YG (Scheme 1) that emitted blue and yellow-green phosphorescence, respectively. Different luminescence of 1B and 1YG resulted from their distinguishing molecular packings. Importantly, polymorph 1B exhibited a phosphorescent mechanochromism phenomenon with a striking contrast in luminescence colors, while polymorph 1YG exhibited a p-RTP effect with a solid-state phosphorescence lifetime of up to 42.80 ms.

Results and discussion

Gold(i) isocyanide complex **1** was prepared according to the described synthesis procedures (Scheme S1[†]), and the structure of the synthesized complex was fully characterized *via* NMR spectroscopy, mass spectrometry, and single crystal X-ray diffraction. Notably, the crystallization of complex **1** by slowly diffusing *n*-hexane vapor into its dichloromethane solution produced two polymorphs **1B** and **1YG** concomitantly.

As shown in Fig. 1, the photoluminescence (PL) spectra of the two types of polymorphs were investigated at room temperature. Polymorph **1B** showed multiple emission peaks in the range of 400–500 nm. Under 365 nm UV light, **1B** was blue emissive with a luminescence quantum yield (Φ) of 17.3%. Furthermore, its PL spectrum was also studied *via* gated measurement with a delay time of 0.1 ms after light excitation.



Scheme 1 (a) Structure of the gold(i) isocyanide complex 1. (b) Single crystal structure of polymorph 1B. (c) Single crystal structure of polymorph 1YG. The insets show the photoluminescence images under 365 nm UV irradiation of two polymorphs 1B and 1YG formed from complex 1.



Fig. 1 (a) Normalized steady-state (solid line) and delayed (dotted line) emission spectra of polymorph **1B** at room temperature. (b) Normalized steady-state (solid line) and delayed (dotted line) emission spectra of polymorph **1YG** at room temperature. (c) Decay curve of **1B** at the peak emission wavelength of 510 nm at room temperature. (d) Decay curve of **1YG** at the peak emission wavelength of 492 nm at room temperature.

Obviously, a red-shifted emission band centred at around 519 nm was observed. The luminescence lifetime of **1B** at the peak emission wavelength of 510 nm was 49.19 μ s. The time-gated luminescence spectrum and the microsecond-level luminescence lifetime of **1B** confirmed its typical room-temperature phosphorescence (RTP) feature.

At 77 K, polymorph 1B showed multiple fine-structure peaks in the range of 400-500 nm, and the delayed emission spectrum of polymorph 1B was similar to its corresponding steady-state emission spectrum (Fig. S1[†]). Furthermore, after mechanical stimulation at room temperature, a new emission peak appeared at 500 nm (Fig. 2a), and the phosphorescent color of 1B changed from blue to green (Fig. 2e). The corresponding Φ value of the obtained green luminescence was 13.2%. Upon fuming the ground sample with dichloromethane vapor for 30 s, the initial blue phosphorescence was recovered. Therefore, 1B exhibited reversible high-contrast phosphorescent mechanochromic behavior. In contrast to 1B, the PL spectrum of the yellow-green-emitting polymorph 1YG showed a broad emission band with two emission peaks at 492 nm and 534 nm and shoulder peaks in the range 400-480 nm (Fig. 1b); the time-gated emission spectrum with a 0.1 ms delay for 1YG was similar to that without a time delay. Moreover, for 1YG, both its steady-state and delayed emission spectra at room temperature were similar to its corresponding steady-state emission spectrum at 77 K. Differing from the steady-state emission spectrum of 1YG at 77 K, the emission peaks in the range of 400-480 nm in the delayed emission spectrum of 1YG at 77 K almost completely disappeared (Fig. S2[†]). Surprisingly, the room temperature phosphorescence lifetime of 1YG at the peak emission wavelength of 492 nm was as high as 42.80 ms, which was about three orders of magnitude longer than that of 1B at 510 nm.



Fig. 2 Normalized steady-state emission spectra of polymorphs **1B** (a) and **1YG** (b) in different states (unground, ground, treated with CH_2Cl_2 vapor). The XRD patterns of polymorphs **1B** (c) and **1YG** (d) in various states. The photographs of polymorphs **1B** (e) and **1YG** (f) in various states taken under 365 nm UV irradiation.

After the removal of the photoexcitation source, a clear yellowgreen RTP lasting several seconds for **1YG** could be directly observed by the naked eye (see Video S1†), thus, demonstrating the p-RTP characteristics. In addition, the polymorph **1YG** also displayed mechano-responsive phosphorescence involving an inapparent color change from yellow-green ($\Phi = 19.7\%$) to green ($\Phi = 16.5\%$) (Fig. 2b and f). From the powder X-ray diffraction (XRD) data (Fig. 2c and d), the two crystal forms of complex **1** exhibited distinctly different structures, and the observed phosphorescent mechanochromism phenomena of **1B** and **1YG** resulted from the morphological transition between the crystalline and amorphous states.

To further understand the p-RTP phenomenon of polymorph 1YG, the time-resolved emission spectra (TRES) of 1YG were investigated. From Fig. 3a, it can be seen that the emission peaks in the range 400-450 nm disappeared on stopping photoexcitation. The maximum emission peak was located at 492 nm with a shoulder peak at 526 nm, which could be assigned to p-RTP emission. Two weak emission peaks were still present even after about 600 ms (Fig. 3b), which was consistent with the fact that the yellow-green phosphorescence could still be seen with the naked eye after removal of the excitation light (Fig. 3c). Interestingly, upon mechanical grinding, the emission peaks for **1YG** at short wavelengths (400-480 nm) disappeared, and the phosphorescent peaks at long wavelengths (480-580 nm) remained basically unchanged (Fig. 2b). In contrast, the luminescence lifetime of 1YG at 507 nm sharply decreased to 4.97 µs after grinding (Fig. S6a[†]). After removing the 365 nm UV lamp, the ground 1YG did not show



Fig. 3 (a) Transient emission spectra of polymorph **1YG**. (b) Transient PL decay image of polymorph **1YG**; the color change from red to blue indicated the decrease of emission intensity. (c) Schematic diagram for mechanically regulated p-RTP of **1YG**.

afterglow emission (see Video S2†). These results indicated that polymorph **1YG** is a mechanically regulated p-RTP crystalline material, and its "on–off" p-RTP effect could be effectively mediated *via* mechanical stimulation.

To obtain deeper insight into the effect of intermolecular interactions on the emission properties of **1B** and **1YG**, the crystal packings of the two polymorphs **1B** and **1YG** were systematically analyzed. As illustrated in Fig. 4, the shortest Au…Au distance between adjacent molecules was 4.745 Å (**1B**) and 4.653 Å (**1YG**), respectively, indicating no significant intermolecular aurophilic interactions.¹⁰ Dipole–dipole interactions were observed between the F atom of pentafluorophenyl and the C atom of the isocyano group in **1YG** (Fig. 4d, *d* = 3.099 Å) or **1B** (Fig. 4b, *d* = 3.174 Å), which promoted intersystem crossing and induced RTP generation.¹¹

Multiple hydrogen-bonding interactions were found in the **1B** and **1YG** crystals (Fig. 5), and these intermolecular forces efficiently impeded their molecular motions and facilitated the molecular packings of **1B** and **1YG**. For **1B**, each molecule was connected to the surrounding molecules through six C–H…F interactions and two C–H…O interactions (Fig. 5a, $d_{H...F}$ = 2.563 Å, 2.606 Å, 2.622 Å; Fig. 5b, $d_{H...O}$ = 2.514 Å), forming a



Fig. 4 (a) The shortest Au···Au distance and $C-H\cdots\pi$ interactions in polymorph **1B**. (b) Dipole–dipole interaction in polymorph **1B**. (c) The shortest Au···Au distance and C–H··· π interactions in polymorph **1YG**. (d) Dipole–dipole interaction in polymorph **1YG**.



Fig. 5 (a) Intermolecular C-H…F interactions in polymorph 1B. (b) Intermolecular C-H…O interactions in polymorph 1B. (c) Intermolecular C-H…F interactions in polymorph 1YG. (d) Intermolecular C-H…O interactions in polymorph 1YG.

loose 3D molecular arrangement. Under the stimulation of a mechanical force, the loose packing motif was broken, and the ordered crystalline state was converted into a chaotic amorphous state. As a result, **1B** exhibited a high-contrast phosphorescent mechanochromic behavior. As for **1YG**, stronger hydrogen-bonding interactions (Fig. 5c, $d_{\text{H}\dots\text{F}} = 2.540$ Å, 2.543 Å, 2.546 Å; Fig. 5d, $d_{\text{H}\dots\text{O}} = 2.424$ Å), C–H··· π interactions (Fig. 4c, d = 2.707 Å) and dipole–dipole interactions (Fig. 4d, d = 3.099 Å) were observed in the crystal. These strong intermolecular interactions resulted in a firm crystal packing, which greatly restrained the nonradiative decay of triplet excitons. Indeed, the nonradiative transitions of **1YG** were effectively restricted by multiple intermolecular interactions, which stabilized the triplet excitons. In comparison with **1B**, the long-lived RTP effect of **1YG** is possibly due to the facilitation

of the intersystem crossing process and the formation of a more stable excited triplet state.

Conclusions

In summary, we successfully prepared two types of crystalline materials 1B and 1YG exhibiting blue and yellow-green phosphorescence respectively from a single gold(1)-containing complex by taking advantage of structural polymorphism. Furthermore, polymorph **1B** exhibited phosphorescent mechanochromic behavior involving a high-contrast color change from blue to green, while polymorph 1YG exhibited a p-RTP effect. Furthermore, an "on-off-on" effect of p-RTP could be effectively achieved by successive treatment via mechanical grinding and solvent fuming. Compared with 1B, the more abundant intermolecular interactions and more rigid conformations of 1YG played a key role in promoting intersystem crossing and suppressing nonradiative decay and thus promoting the occurrence of the notable p-RTP phenomenon. To the best of our knowledge, this is the first report describing two types of crystalline materials with high-contrast phosphorescent mechanochromism or p-RTP behavior from a single luminogen. The structural polymorphism strategy demonstrated here may open up a new avenue for realizing p-RTP and high-contrast mechanochromism.

Conflicts of interest

There are no conflicts to declare.

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