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Mismatched changes of the photoluminescence and crystalline structure of a mechanochromic gold(I) isocyanide complex

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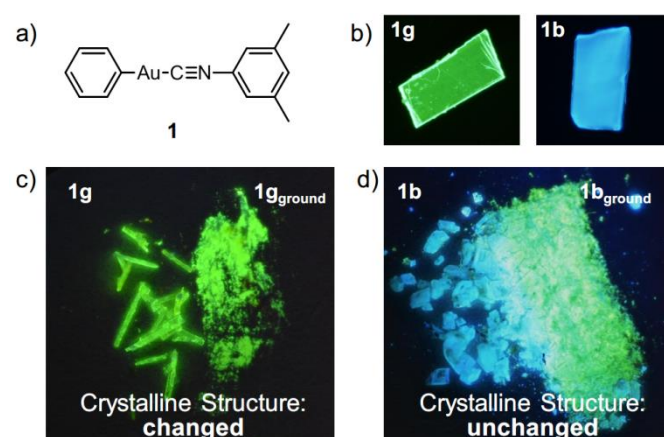
Mechanochromic compound 1 forms green-emitting crystals (1g) and blue-emitting crystals (1b) that exhibit two intriguing responses to mechanical stimulation. Upon mechanical stimulation, the emission color of 1g does not change but its crystalline structure does. Conversely, 1b shows a clear emission shift, but it retains its molecular arrangement upon grinding.

Studies of luminescent mechanochromic compounds based on organic and organometallic compounds are currently considered important because of their wide possible applicability in sensing and recording devices.¹ In these systems, mechanical force, such as grinding, pressing, shearing, and ball milling, alters molecular arrangements in the solid phase and thus changes intermolecular interaction patterns. As a result, solid-state photoluminescence properties can be switched by mechanical stimulation.² Because emission is strongly correlated with solid-state structure, most mechanochromic compounds show changes of both emission behavior and crystalline structure upon mechanical stimulation. In particular cases, mechano-induced emission color changes occur because of minor alterations in crystalline structure in which the overall molecular arrangements of the materials are retained.³ However, there are few examples of such mismatches in the magnitude of changes between emission profiles and crystalline structures upon grinding.³

We previously reported⁴ a mechano-triggered single-crystal-to-single-crystal (SCSC) phase transition with a corresponding change in the emission profile of gold(I) isocyanide complex **1**, a unique class of mechanochromism.⁵ Weak mechanical stimulation on a local area of green-emitting single crystal **1g** readily induces phase transition of the local area. This local phase change gradually occurs over the entire crystal spontaneously. As a result, the whole **1g** crystal is transformed into weak blue-emitting single crystal **1b** in an SCSC manner. This is the first example of a mechanically triggered SCSC phase transition.^{4,6} By taking advantage of the SCSC phase transition of **1**, we determined the detailed molecular

arrangements of **1g** and **1b**, and carefully examined the relationship between crystalline structures and emission properties of these materials.⁴ However, we have not reported the strong mechanical stimulation-induced phase transition behavior of **1** with a corresponding emission color change, which is strikingly different from the previously reported behavior.⁴

Herein, we present the unusual mechanochromism of **1g** and **1b**, where the magnitudes of the changes of emission profiles induced by mechanical stimulation are mismatched with the changes in the crystalline structures (Fig. 1). Rapidly crystallized green-emitting **1g** (Fig. 1b) does not show an emission color change upon strong mechanical stimulation (Fig. 1c). Despite the absence of an emission color change of **1g** induced by mechanical stimulation, powder X-ray diffraction (PXRD) studies indicate that the crystalline structure is completely changed to the other crystalline phase. In contrast, slowly crystallized blue-emitting **1b** (Fig. 1b) exhibits a clear emission shift to green upon grinding (Fig. 1d). Despite this mechanochromism of **1b**, PXRD analyses reveal that no crystalline structure change is induced by mechanical stimulation. Detailed investigation indicates that these two mismatches in the magnitude of changes of the photoluminescence and crystalline structures of **1g** and **1b** occur because of energy transfer within ground powder **1g_{ground}** and **1b_{ground}**, respectively.



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Fig. 1 (a) Structure of **1**. (b) Photographs of **1g** and **1b** under UV light ($\lambda_{\text{ex}} = 365$ nm). Photographs of emission color changes (c) from **1g** to **1g_{ground}** and (d) from **1b** to **1b_{ground}** upon strong grinding by a pestle on glass substrates ($\lambda_{\text{ex}} = 365$ nm).

Complex **1** shows an intriguing emission color change upon strong mechanical stimulation. Rapid and slow crystallization of **1** from dichloromethane/hexane afforded green- and blue-emitting crystals **1g** and **1b**, respectively (Fig. 1b).⁷ Single-crystal structure analyses indicated that crystallized **1g** and **1b** are identical to the previously reported single crystals of **1**, between which a mechano-triggered SCSC phase transition occurred.^{4,8} Strong grinding of a **1g** crystal with a pestle did not induce a prominent emission color change (Fig. 1c). In contrast, strong grinding of **1b** induced a substantial emission color change to green (Fig. 1d). When **1g** and **1b** were strongly stimulated by ball milling for 30 min at 4600 rpm, the same emission changes were also observed. The resulting ground phases **1g_{ground}** and **1b_{ground}** exhibited identical emission spectra (Figs. 2a and b and S1 and S2). Remarkably, the changes in the emission profiles of **1** upon strong grinding are completely opposite to that observed for the previously reported mechano-triggered SCSC phase transition from **1g** to **1b**, in which emission color changed from green to blue.⁴ In our previous work, a small mechanical stimulus was applied at a local area of a **1g** crystal and thus the resulting **1b** was also a crystal.⁴ Meanwhile, in this study, strong mechanical stimulation was applied to the crystals, so the powder forms **1g_{ground}** and **1b_{ground}** were obtained.

We measured the optical properties of **1g** and **1b**. Green-emitting **1g** showed a broad emission spectrum peaking at 535 nm upon excitation at 370 nm (solid green line in Fig. 2a). The excitation spectrum of **1g** exhibited a broad band extending to around 450 nm (solid green line in Fig. 2c). The absolute emission quantum yield (Φ_{em}) and average lifetime τ_{av} [$= (\sum A_i \tau_i) / (\sum A_i)$] of **1g** were 84% and 0.97 μs , respectively (Fig. S3 and Table S1). Meanwhile, blue-emitting **1b** showed a structured emission band with maxima at 422, 457, and 489 nm (solid blue line in Fig. 2d).⁹ The excitation maximum of **1b** ($\lambda_{\text{em}} = 445$ nm) was located at 312 nm (solid blue line in Fig. 2d). Both emission and excitation spectra of **1b** appeared shorter wavelength than those of **1g**, and **1b** showed τ_{av} of 12.9 μs and Φ_{em} of 33% (Table S1).

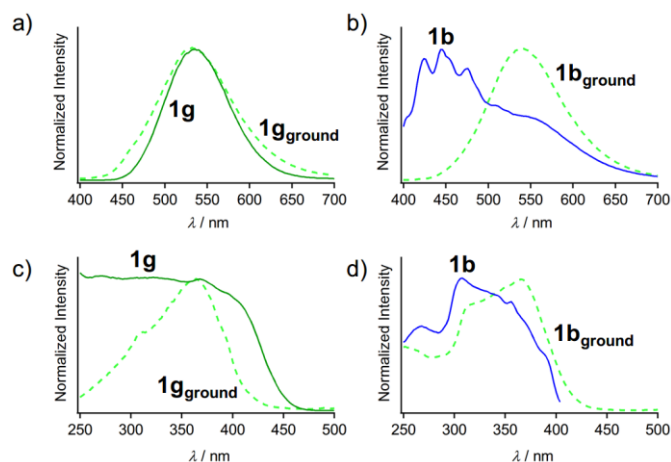


Fig. 2 Emission spectral changes of (a) **1g** (solid green line) to **1g_{ground}** (dashed light green line) and (b) **1b** (solid blue line) to **1b_{ground}** (dashed light green line) by mechanical stimulation ($\lambda_{\text{ex}} = 370$ nm). Excitation spectral changes of (c) **1g** (solid green

line) to **1g_{ground}** (dashed light green line) and (d) **1b** (solid blue line) to **1b_{ground}** (dashed light green line) by mechanical stimulation ($\lambda_{\text{em}} = 535$ nm; only for **1b**, $\lambda_{\text{em}} = 445$ nm).

We next investigated the optical properties of **1g_{ground}** and **1b_{ground}** and compared them with those of **1g** and **1b**, respectively. The emission spectra of **1g_{ground}** and **1b_{ground}** are identical to each other, consisting of structureless emission bands with maxima at 539 nm (Figs. 2a and b and S1). These maxima are almost identical to that of **1g** (535 nm), indicating that the **1g** crystal did not show mechanochromism. Despite the absence of emission spectral changes when **1g** was transformed to **1g_{ground}** (Fig. 2a), their excitation spectra are slightly changed (Fig. 2c), which may indicate that their photoluminescence processes are different. In contrast, emission bands exhibited a red shift of 78 nm upon the phase transition from **1b** to **1b_{ground}** (Fig. 2d), indicating that **1b** is a mechanochromic material. Despite the complete shift in emission when **1b** was transformed to **1b_{ground}** upon grinding, **1b_{ground}** has a remaining excitation shoulder at 313 nm which is corresponding to the excitation maximum of **1b** (Fig. 2d).¹⁰ Not only the excitation and emission spectra but also other photophysical properties are changed when **1g** $\rightarrow$ **1g_{ground}** and **1b** $\rightarrow$ **1b_{ground}** transitions occur. For example, the τ_{av} values of **1g_{ground}** and **1b_{ground}** are around 0.8 μs (Fig. S3 and Table S1), which are similar to that of **1g** (0.970 μs) and much shorter than that of **1b** (12.9 μs). In addition, Φ_{em} of **1g_{ground}** and **1b_{ground}** are around 20%, smaller than those of **1g** and **1b** (Table S1).

Interestingly, PXRD analyses indicated that mechano-induced change profiles of crystalline structures of **1** are mismatched from those of photoluminescence. PXRD patterns of **1g_{ground}** and **1b_{ground}** are identical to each other and showed intense diffractions (lower lines in Fig. 3a and b).¹¹ The upper lines in Fig. 3a and b are simulated powder patterns of **1g** and **1b**, respectively, based on the single crystalline structures.⁴ The PXRD pattern of **1b_{ground}** is similar to the simulated pattern of **1b** (Fig. 3b). This indicates that molecular arrangements of **1b** and **1b_{ground}** are similar, which is further supported by their UV/vis absorption spectra (Fig. S4). This suggests that the crystalline structure of **1b** is almost unchanged upon grinding (Fig. 3b) despite its marked change in emission properties (Fig. 1d). Conversely, mechanical grinding of **1g** induced dramatic crystalline structure changes into a phase similar to that of **1b** (Fig. 3a), even though emission color barely changed (Fig. 1d).

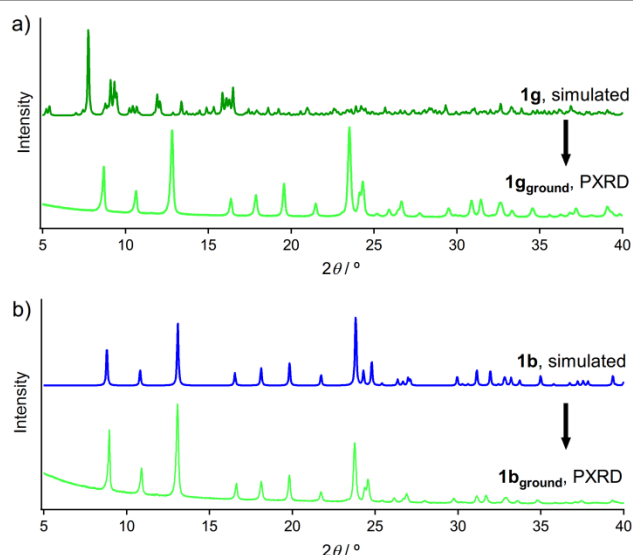


Fig. 3 (a) Simulated powder patterns of **1g** and **1b** derived from single-crystal structures [upper lines in (a) and (b), respectively] and PXRD patterns of **1g_{ground}** and **1b_{ground}** [lower lines in (a) and (b), respectively].

The green emission of **1g_{ground}** and **1b_{ground}** is suggested to occur via energy transfer from blue- to green-emitting crystalline domains within the powder (Fig. 4, middle).¹² PXRD analyses indicate that the molecular arrangements of both **1g_{ground}** and **1b_{ground}** are similar to that of blue-emitting **1b** (Fig. 3); however, both **1g_{ground}** and **1b_{ground}** exhibited green emission similar to that of **1g** (Fig. 1). This indicates that both **1g_{ground}** and **1b_{ground}** must contain small amounts of green-emitting crystalline domain **1g** within the main **1b** crystalline domain (Fig. 4, middle). It is believed that this minor **1g** domain within **1g_{ground}** or **1b_{ground}** is responsible for the overall green emission followed by energy transfer from the main **1b** crystalline domain. The dominant emission of minor crystalline domains of mechanochromic compounds has been reported previously.^{3a,b} For example, Zhang reported that mechanical stimulation to a mechanochromic compound produces small amount of the new crystalline domain which is responsible for the photoluminescence of the resulting ground powder because of the energy transfer from the remaining original crystalline domain.^{3b} In the present study, the following several experimental findings indicate that this process occurs in **1**. For example, the emission decay profiles of **1g** and **1g_{ground}** (and **1b_{ground}**) are quite similar (Fig. S3), indicating that their excited-state species involved in photoluminescence are identical. The lower Φ_{em} of **1g_{ground}** and **1b_{ground}** than those of **1g** and **1b** are caused by quenching of the excited state through energy transfer (Table S1).¹³

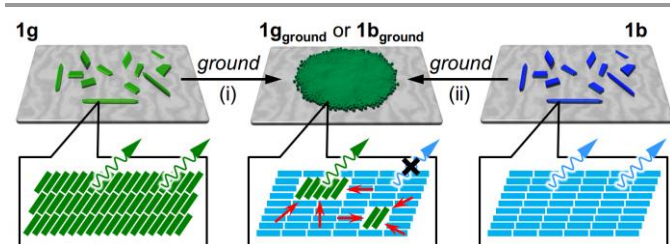


Fig. 4 Top: schematic representations of mechanochromism of **1g** into **1g_{ground}** (from left to center) and **1b** into **1b_{ground}** (from right to center). Bottom: schematic representations of the corresponding molecular arrangements in which green and blue rectangles

represent **1** molecules in **1g** and **1b**, respectively. Because of energy transfer events (red arrows), **1g_{ground}** and **1b_{ground}** exhibited green emission similar to that of **1g** even though the molecular arrangement is similar to that of **1b**.

On the one hand, for the **1g** → **1g_{ground}** phase transition induced by strong grinding, the emission color is unchanged [Fig. 4, (i)]. On the other hand, emission color is changed to blue as a result of the previously reported **1g** → **1b** SCSC phase transition by weak mechanical stimulation;⁴ this difference is likely because the **1g_{ground}** phase exhibits more efficient energy transfer than SCSC-produced **1b**. Despite the different emission properties of the **1g_{ground}** powder (green emission) and single crystal **1b** obtained by the SCSC phase transition (blue emission),⁴ their crystalline structures are identical to each other. As previously reported, even a blue-emitting single crystal **1b** prepared by the mechano-triggered SCSC phase transition of **1g** has a residual **1b** domain that participates in energy transfer.⁴ Thus, the emission spectrum of the resulting single crystal **1b** exhibited a residual green emission band as well as a newly emerged blue emission band.⁴ The **1g_{ground}** powder obtained by strong grinding has a less ordered molecular arrangement and smaller particle size than single crystal **1b**,⁴ which may facilitate energy transfer in **1g_{ground}** and thus no residual blue emission band from the main crystalline domain was observed for **1g_{ground}** (Fig. 2a).

The **1b** → **1b_{ground}** phase transition with a blue-to-green emission color change induced by strong grinding [Fig. 4, (ii)] is surprising because X-ray diffraction studies revealed there was no marked change in crystalline structure (Fig. 3b).³ We believe this shift of emission is caused by the formation of a small amount of a kinetically trapped **1g** crystalline domain within **1b_{ground}** when **1b** phase is mechanically stimulated. One possible evidence for this “reverse mechanochromism” in a local area in **1b_{ground}**; however, the appearance of an excitation maximum at 365 nm for **1b_{ground}** obtained by grinding **1b** (light green line in Fig. 2d) may support the emergence of a small **1g** domain within **1b_{ground}**.

In summary, we reported two different mismatched changes in the structure and emission profiles of mechanochromic complex **1**, in which **1g** exhibited no change of emission color but a prominent structural change upon mechanical stimulation, whereas **1b** showed a clear change of emission color but a similar overall crystalline structure. We proposed that these complicated changes of emission and crystalline structures upon mechanical stimulation are caused by energy transfer within ground powders **1g_{ground}** and **1b_{ground}**. Although mechanochromism with retention of the overall crystalline structure has been observed,³ a change in the crystalline structure of the same compound without alteration of emission properties upon grinding is unprecedented.

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 - 8 See reference 4 for a detailed discussion on the crystalline structures and their relationship with emission. Briefly, single crystalline structure of **1g** contains aurophilic interactions whereas that of **1b** does not contain aurophilic interactions. In general, the formation of aurophilic interaction resulted in the red-shifted emission band. Therefore, longer wavelength emission of **1g** ($\lambda_{\text{em,max}}$ = 535 nm) than that of **1b** ($\lambda_{\text{em,max}}$ = 445 nm) is caused by the formation of the aurophilic interaction in the single crystal structure of **1g**.
 - 9 These bands are almost consistent with the emission bands of mechanically obtained single crystal **1b** in a shorter wavelength region; see reference 4 for more detail.
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