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Mechanical Path to a Photogenerated Structure: Ball Milling-Induced Phase Transition of a Gold(I) Complex

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Ball milling of blue-emitting crystal 1B of gold(I) isocyanide complex 1 induces a phase transition to yellow-emitting powder 1Y_G, which has the same solid structure as previously reported 1Y obtained upon photoirradiation of 1B. This is the first example of mechanical stimulation inducing a phase change to a photo-accessible crystalline phase.

Photochromic materials have attracted much attention because of their great possibility for application in sensors, memory devices, and bioimaging.¹ The optical property switching of photochromic materials is induced by molecular structure changes induced by photochemical reactions such as photocyclisation, photoelimination, and photoisomerisation.² Because the photochemical reactions proceed through a photoinduced excited state, these reactions and structure changes usually give unique results that are different from those obtained by thermal reactions, as exemplified by the Woodward–Hoffmann rule. It is generally difficult to make a photochromic compound show a similar chromotropic change by another type of external treatment such as temperature change or static pressure application.

Recently, chemical³ and crystal structure⁴ transformation induced by mechanical force have received interest in view of development of efficient synthetic methods as well as their application in mechanical sensors and recording materials. Applying mechanical force was found to induce an interesting reaction pattern that cannot be achieved by classical heating, or applying hydrostatic pressure.³ This is explained by anisotropic mechanical force affecting covalent bonds in molecules, intermolecular interactions, or molecular assemblies in a different way from that of heating and hydrostatic pressure. A solid chromic material where both photoirradiation and mechanical stimulus induce the same new emission properties and polymorph structure has not been reported.

Here, we found that ball milling of blue-emitting crystals (1B) of gold(I) isocyanide complex 1 induces a crystal-to-crystal (CC) phase transition to yellow-emitting powder 1Y_G. This powder has the same structure as the photogenerated yellow-emitting phase 1Y, which we could previously only obtain through photoinduced single-crystal-to-single-crystal (SCSC) phase transition of 1B crystals (Fig. 1).⁵ The optical properties of 1Y_G are also same as those of 1Y crystals. The phase change from 1B to 1Y does not proceed by thermal treatment or hydrostatic pressure. This is the first case of a mechanical stimulus-induced CC phase transition to another crystal phase that is same as the phase generated by photoirradiation.

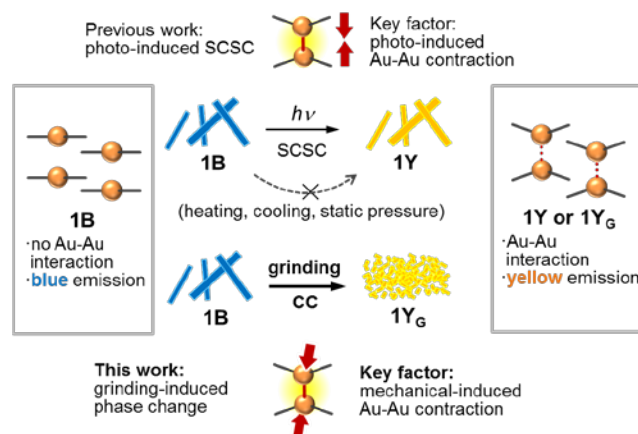


Fig. 1 Schematic illustration of mechano-induced phase transition of 1 to a photo-accessible crystalline phase.

We previously reported that gold(I) isocyanide complex 1 (Fig. 2a) displays a photoinduced SCSC phase transition that involves the shortening of intermolecular auophilic bonds.⁵ Upon strong ultraviolet (UV) irradiation of blue-emitting crystals 1B, the emission colour changed to yellow (1Y, Fig.

2c). X-ray diffraction (XRD) analyses revealed that SCSC phase transition occurred upon photoirradiation and the distance between Au atoms of adjacent molecules shortened from 3.501(14) Å to 3.2955(6) Å (Fig. 2b). We proposed that this phase change proceeded through the shortening of the intermolecular Au-Au distance in the photoexcited state based on density functional theory calculations and the structure analyses.

The ball milling of **1B** can achieve a similar phase change that was observed after photoirradiation of **1B**. Crystals of **1B** exhibited blue emission under weak UV irradiation with the emission maximum at 450 nm (Fig. 2e, blue solid line). Ball-milling **1B** crystals for 30 min at 4600 rpm afforded yellow-emitting powder **1Y_G**, (Fig. S3). The optical properties of the **1Y_G** powder are similar to those of previously reported **1Y** crystals. **1Y** crystals were prepared through SCSC phase transition induced by exposure of **1B** crystals to strong UV irradiation (367 nm, ca. 100 mW·cm⁻²) for 1 min.⁵ **1Y** displayed a broad emission spectrum with the emission maximum at 590 nm (Fig. 2e, yellow solid line). The **1Y** emission resembles the emission spectrum of **1Y_G** (Fig. 2e, black solid line) although it has remaining small shoulder around at 470 nm. The emission lifetime τ_{av} of **1Y_G** (τ_{av} = 1.177 μ s) was also similar to that of **1Y** (τ_{av} = 0.685 μ s, Fig. S1 and Table S1). Although preparation methods of **1Y_G** and **1Y** are different, these similar optical properties indicate that the emission process of the **1Y_G** powder is identical to that of a **1Y** crystal. Thermal analyses using a thermography camera confirmed that mechano-generated friction heat was negligible (less than 5 °C, Fig S3). Elemental analyses and ¹H NMR measurements revealed that no solvent was included in **1B** and **1Y_G** (Fig. S4 and Table S2). These results also indicate that chemical decomposition of the complex did not occur after grinding. Attempts to reverse the emission colour change from yellow **1Y_G** to blue **1B** by heating or solvent contact were not successful, indicating that the **1Y_G** is more thermodynamically stable than **1B**.^{4b}

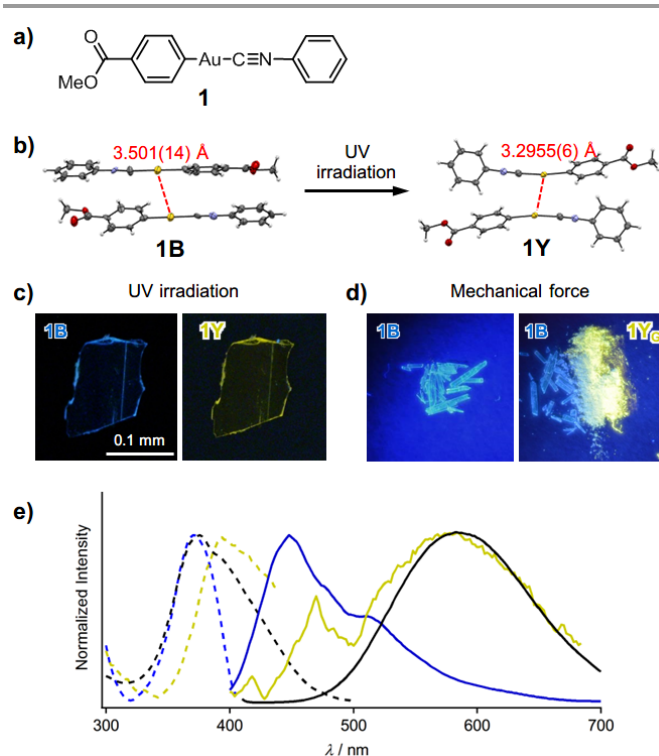


Fig. 2 a) Chemical structure of **1**. b) Single-crystal structures of **1B** and **1Y**. c), d) Photographs of the emission colour change of **1B** upon c) UV irradiation and d) ball milling, respectively. e) Normalised excitation (**1B**: blue dashed line, detected at 450 nm; **1Y**: yellow dashed line, detected at 590 nm; **1Y_G**: black dashed line, detected at 590 nm) and emission spectra (**1B**: blue solid line, λ_{ex} = 370 nm; **1Y**: yellow solid line, λ_{ex} = 390 nm; **1Y_G**: black solid line, λ_{ex} = 390 nm).

Powder XRD analysis revealed that the crystal structure of **1Y_G** is identical to that of **1Y**. The simulated diffraction pattern of **1B** derived from the single-crystalline structure was dramatically different from that of **1Y_G** (Fig. 3, blue and black lines, respectively). The intense peak at 7.90° in addition to other weaker peaks almost disappeared and new peaks appeared after ball milling, indicating the change in the molecular arrangement. Therefore, the mechano-induced CC phase transition from **1B** to **1Y_G** takes place. The majority of the structure changes observed for mechanochromic compounds are from crystalline to an amorphous phase;⁴ CC phase transition is rare.⁶ The diffraction pattern of **1Y_G** is rather weak in intensity but very similar in positions to the simulated diffraction pattern of **1Y** (Fig. 3, yellow line), confirming that their crystalline structures are identical.⁷

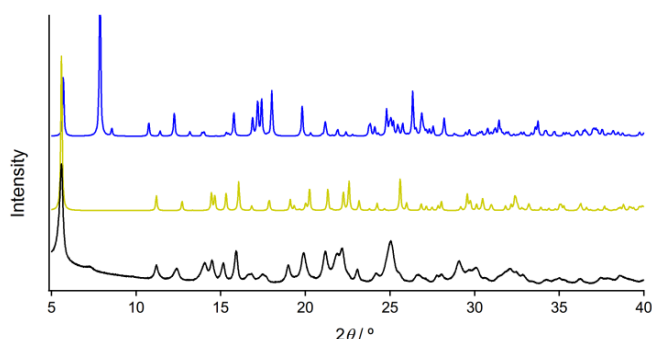


Fig. 3 Powder XRD pattern of **1Y_G** (black line) and simulated powder patterns of **1B** (blue line) and **1Y** (yellow line) derived from the corresponding single-crystalline structures.

Ball milling can probably afford the photo-accessible crystalline phase of complex **1** because the effects of grinding and photoirradiation on the intermolecular interactions in **1** are similar. Both stimulation methods induce intensification of aurophilic interactions and shortening of the distance between Au atoms, promoting the phase transition from **1B** to **1Y** (Fig. 4).⁵

Photoirradiation of **1B** resulted in stronger aurophilic interactions. The highest occupied molecular orbital (HOMO) has anti-bonding character for the Au–Au interactions.⁸ One-electron excitation from the HOMO to the higher unoccupied orbital decreases the anti-bonding character, so the aurophilic interactions became stronger in the excited state (Fig. 4a).⁹ Then, SCSC transformation from the photogenerated transient structure **1X_p** to **1Y** occurred (Fig. 4b). In this photoinduced phase transition, the molecular-scale internal force formed between Au atoms would drive the macroscopic phase change of crystals.

It is expected that mechanical stimulation of organic crystals forces the molecules closer together and intensifies intermolecular interactions, similar to many mechanochemical reactions,¹⁰ unless the phase change is accompanied with marked compound diffusion or structure change (Fig. S5 and S6, and Table S3).¹⁰ The external mechanical forces on the molecules are incoherent in strength and random in their directions. When Au atoms are forced closer together in the transient structure **1X_G** (<3.5 Å) during the grinding process (Fig. 4c), the aurophilic interactions between the Au atoms are strengthened considerably, because aurophilic interactions belong to a class of dispersion force and their strength has R^{-6} dependence (R is the distance between Au atoms).⁶ The stronger aurophilic bonds induced by grinding can promote the phase change to **1Y** (Fig. 4a). In this mechano-induced phase transition, the macroscopic external mechanical force causes a molecular-level structure change with a CC phase transition.

It is noted that other stimulus including heating, cooling, and hydrostatic pressure could not induce the phase change from **1B** to **1Y**. Although some arylgold(I) isocyanide complexes can show temperature dependent phase changes, no phase transitions of **1B** and **1Y** were observed from –150 to 120 °C (Fig. S7–S10). The crystals melted and decomposed

above 121 °C. The emission colour change did not occur upon applying static pressure to **1B** (N_2 gas pressure of 12 MPa in an autoclave for 1 h). It is interesting that photoirradiation and ball milling, which cause anisotropic distortion to the molecules, can induce the phase change of **1**, whereas isotropic stimuli including heating/cooling and hydrostatic pressure could not promote the phase change.

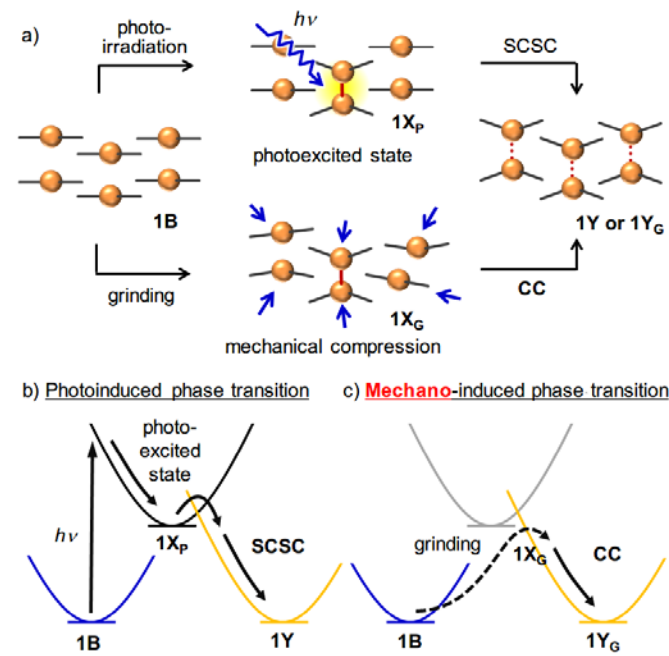


Fig. 4 a) Schematic representations of photoinduced and mechano-induced phase transitions of **1B**. b) Schematic representation of energy diagrams of **1** showing c) the photoinduced and d) mechano-induced phase transitions of **1B** to **1Y**.

We have reported the mechano-induced CC phase transition to a photo-accessible crystalline phase of complex **1**. Upon ball milling of blue-emitting **1B** crystals), CC phase transition occurs and yellow-emitting powder **1Y_G** is obtained. The optical properties and crystalline structures of the **1Y_G** powder are similar to those of **1Y** crystals obtained through photoinduced SCSC phase transition of **1B** crystals. We believe this is the first example of a mechano-induced CC phase transition to a crystalline phase that is also obtained through photoinduced phase transition. The similar effects of mechanical stimulation and photoirradiation on the intermolecular interactions in **1** cause the mechano-induced CC phase transition to give a photo-accessible crystalline phase.

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† Electronic Supplementary Information (ESI) available: Experimental procedures, emission decay profiles, DSC profiles, and Crystal structures. See DOI: 10.1039/c000000x/

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