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Low-Temperature-Selective Luminescent Mechanochromism of a Thienyl Gold Isocyanide Complex

Tomohiro Seki,* Koh Kobayashi, Hajime Ito*

The low-temperature-selective mechanochromism of a thienyl gold(I) isocyanide complex is reported. The as-prepared powder of this complex did not show any luminescent color changes upon grinding at room temperature. When cooled below −50 °C, the powder showed a blue emission in the absence of a phase transition. Upon grinding this powder below −50 °C, a green emission was observed, which indicates notable mechanochromism that only occurs at low temperature.

Studying phase transitions of organic crystalline materials is important both from a fundamentally scientific perspective, as well as with regard to applications in a variety of areas including materials sciences and the pharmaceutical industry. One important reason to study phase transitions in organic crystalline materials is that such transitions often result in a modification of the optoelectronic properties of the materials, which in turn depend in general on the molecular arrangements. Thermally induced phase transitions of organic compounds are well established, but the study of mechanically induced phase transitions is a more recent phenomenon that has received increased interest. Especially luminescent mechanochromism, in which mechano-induced phase transitions result in changes of the photoluminescent properties of a material, have attracted much attention in this decade. One unique aspect of mechano-induced phase transitions is that the phases obtained after mechanical stimulation cannot be obtained by other stimuli including temperature changes.

In general, mechanochromic emission-color changes upon mechanical treatment have been investigated at room temperature, and temperature-dependent mechanochromic behavior has so far been seldomly discussed. Ramamurty and Reddy have reported that the mechanochromic behavior of a difluoroboron complex at low temperature is slightly different from that at room temperature; however, a detailed mechanism was neither presented nor proposed. Moreover, it has been reported that mechanical stimulation at ambient temperature and at ~100 °C can induce distinct changes of the emission-color profile of a liquid-crystalline and a solid compound. We have intensively studied a series of aryl gold isocyanide complexes, as the structures and emission colors of compounds with aryl gold isocyanide moieties are extremely sensitive to mechanical and other stimuli. During our studies, we discovered that thienyl gold isocyanide complex (Fig. 1) exhibited mechanochromic properties exclusively at low temperatures. To the best of our knowledge, selective luminescent mechanochromism at low temperature has so far been unprecedented.

Herein, we report the low-temperature-selective mechanochromism of 1. The as-prepared form of 1 (1R) shows red emission, which is retained upon mechanical stimulation at room temperature, indicating the absence of mechanochromism at this temperature. Upon decreasing the temperature, an emission-color change of 1R occurs to afford blue-emitting 1RBlue. Powder and single-crystal X-ray
diffraction (XRD) analyses indicated that this emission-color change should be caused by thermal contraction of the crystalline lattice, rather than by a phase transition. In stark contrast to the behavior at ambient temperature, grinding \textbf{1R}_{\text{blue}} below \(-50\) °C induced a dramatic emission-color change to green, on account of the formation of \textbf{1G}. The key factor for the low-temperature-selective mechanochromism of \textbf{1} is the distinct temperature-dependent relative thermodynamic stability of \textbf{1R} and \textbf{1G}.

At room temperature, \textbf{1} does not exhibit luminescent mechanochromism. The preparation of \textbf{1} was accomplished according to a previously reported procedure (cf. ESI).\textsuperscript{10b} The pristine powder of \textbf{1} obtained after reprecipitation (\textbf{1R}) exhibited a red emission (\(\lambda_{\text{ex}} = 365\) nm) with an absolute emission quantum yield (\(\Phi_{\text{em}}\)) of 0.02 under UV excitation (Fig. 1).\textsuperscript{13} Upon heating to 110 °C, \textbf{1R} decomposes in the absence of a thermal phase transition (Fig. S2). The photoluminescence spectrum of \textbf{1R} ranges from 400–800 nm with maxima at 463, 591, and 626 nm (red line in Fig. 2). Upon grinding \textbf{1R} (Fig. 1i), the emission color of the powder (\textbf{1R})' hardly changed. In addition, spectral changes of the emission were not observed (black line in Fig. 2), indicating the absence of mechanochromism of \textbf{1} at room temperature.

Upon cooling \textbf{1R}, its emission color changed from red to blue. When \textbf{1R} was cooled on a cooling/heating stage, its emission color gradually changed and a blue emission was observed below \(-50\) °C (Fig. 1ii). Further cooling of this solid (\textbf{1R}_{\text{blue}}) to \(-150\) °C did not induce another emission-color change, albeit that the emission intensity increased (Fig. S3). The emission color of \textbf{1R} and \textbf{1R}_{\text{blue}} is reversible: the original red emission of \textbf{1R} was recovered upon warming \textbf{1R}_{\text{blue}} to \(-50\) °C (Fig. 1iii). The emission spectrum of \textbf{1R}_{\text{blue}} (Fig. 2) shows peaks at \~460 nm (\(\Phi_{\text{em}} = 0.34\)). Additional emission maxima of \textbf{1R}_{\text{blue}} at 591 and 626 nm were also observed in the emission spectrum of \textbf{1R} (Fig. 2). Similarly, the excitation spectrum of \textbf{1R}_{\text{blue}} is well matched to that of \textbf{1R} (Fig. S4).

Upon grinding \textbf{1R}_{\text{blue}} below \(-50\) °C, a dramatic color change of the emission from blue to green was observed. Upon cooling under a nitrogen atmosphere,\textsuperscript{13} \textbf{1R} initially transformed to blue-emitting \textbf{1R}_{\text{blue}} before it was mechanically stimulated with a spatula at \(-75\) °C. Then, we observed a clear emission-color change from blue to green (Fig. 1iv) of the resulting powder (\textbf{1G}). This mechanochromism was observed exclusively below \(-50\) °C. Remarkably, \textbf{1G} cannot be obtained from cooling \textbf{1R} (Fig. 1v), which suggests that mechanical stimulation at low temperature is required to obtain \textbf{1G}. The ground powder of \textbf{1G} shows an emission spectrum with a peak at 540 nm (Fig. 2), which suggests a mechano-induced bathochromic shift. Although the green emission of \textbf{1G} (\(\Phi_{\text{em}} = 0.41\)) remains intact at low temperature, it transforms into a red emission at \(-10\) °C, implying the recovery of \textbf{1R} (Fig. 1vi). The recovery of \textbf{1R} is also supported by the spectral changes of the emission of \textbf{1G} upon heating (Fig. S6).\textsuperscript{14} This result indicates that \textbf{1R}_{\text{blue}} cannot be recovered from the mechanically obtained \textbf{1G}.

In order to understand the complicated mechano-induced emission-color changes of \textbf{1}, we analyzed the molecular arrangements. First, we examined the single-crystal XRD structures of \textbf{1R} and \textbf{1R}_{\text{blue}}, which are in essence identical. Upon crystallization of \textbf{1} from \(\text{CH}_3\text{Cl}_2/\text{hexane}\), red-emitting single crystals of \textbf{1R} (Fig. 3) were obtained, whose emission spectral features correspond well to those of the powder of \textbf{1R} (Fig. S7). Subsequently, a single-crystal XRD analysis was carried out at room temperature to evaluate the molecular arrangement of \textbf{1R}. \textbf{1R} crystallizes in the triclinic space group \(P\-1\) (Figs. 3 and S8 and Table S1). The thienyl ring is rotationally disordered (Fig. 3), which is common for thiophene compounds.\textsuperscript{15} The molecular arrangements are relatively simple and consist of head-to-tail arrangements that form aligned 1-D columns (Fig. 3). In these head-to-tail arrangements, multiple \(\text{CH}_3/\text{C}_6\) interactions were observed. The thienyl and phenyl rings in \textbf{1R} include dihedral angles (\(\theta_{\text{dihedral}}\)) of 69.0°. Subsequently, the same single crystal was cooled to \(-150\) °C, and the emission color gradually changed to blue (Fig. S9), indicating the formation of \textbf{1R}_{\text{blue}}.\textsuperscript{16} The diffraction data of this blue-emitting single crystal were collected at \(-150\) °C, and showed that the structure of \textbf{1R}_{\text{blue}} is similar to that of \textbf{1R} (Fig. S8 and S11 and Table S1), although a small contraction of the crystalline lattice was observed, i.e., the volume contracted from 551.1(5) to 532.54(15) \(\text{Å}^3\). This result indicates that a thermal phase transition should not occur between \textbf{1R} and \textbf{1R}_{\text{blue}}.\textsuperscript{17}
The powder XRD analyses of 1R, 1R', 1R\textsubscript{Blue}, and 1G indicated the mechanical generation of a new crystalline phase at low temperature. Initially, samples of reprecipitated 1R exhibited powder XRD patterns with intense peaks, consistent with the crystalline nature of 1R. This pattern was almost completely reproduced by simulations of the powder pattern of the red-emitting single crystal \textit{vide supra}, Fig. S13. Then, we recorded the powder XRD pattern of the ground powder 1R at room temperature. 1R' exhibited a powder XRD pattern that is virtually identical to that of 1R (Fig. 4). This result suggests that a crystalline structure change does not occur upon grinding 1R at room temperature, which is consistent with the absence of mechanochromism. At −150 °C, 1R\textsubscript{Blue} exhibited a powder XRD pattern that is slightly different from that of 1R (Fig. 4). Further variable-temperature powder XRD analyses showed gradual peak shifts (Fig. S14), which support the notion of the absence of a thermal phase transition. 18 Subsequently, we obtained a powder sample of 1G from the mechanical stimulation of 1R\textsubscript{Blue}. 19 1G exhibited a powder pattern similar to that of 1R\textsubscript{Blue}, albeit that intense additional diffraction peaks appeared at 2θ = 22.8, 24.3, and 25.9° (arrows in Fig. 4) together with smaller diffraction peaks (triangles in Fig. 4). This result indicates that a new crystalline phase appeared upon grinding, although the original phase of 1R\textsubscript{Blue} is mostly retained in 1G. This newly formed crystalline phase should be the key to the mechanochromism of 1 at low temperature. If thorough grinding of 1R\textsubscript{Blue} at such low temperatures and transferring the resulting sample to the sample stage while keeping the temperature strictly below −50 °C were possible, more efficient crystalline structure changes into the 1G phase should be detected.

For the green emission of 1G, energy-transfer events should be considered. The powder XRD analyses indicated that the molecular arrangement of green-emitting 1G is rather similar to that of unground blue-emitting 1R\textsubscript{Blue}. To achieve green emission for 1G, energy transfer should occur from the main original crystalline domain to a smaller amount of newly formed crystalline domains. We have previously reported that some gold isocyanide complexes exhibit emission from minor crystalline domains \textit{via} energy transfer from major crystalline domains. 10,20 This notion is supported by the results of emission-lifetime measurements (Fig. S17). An emission decay curve of 1G could not be fitted, indicating a complex emission process, i.e., an energy-transfer process. In contrast, emission decays of 1R and 1R\textsubscript{Blue} can be reasonably fitted as bi- and triexponential curves, respectively (Fig. S17 and Table S2).

When we mechanically stimulated 1R at temperatures between 0 °C and −25 °C, “transient” emission-color changes from red to green were observed, before red-emitting 1R was spontaneously recovered within minutes. At 0 °C, mechanical stimulation of 1R induces the emergence of a green-emitting phase that is similar to 1G, and the red emission is spontaneously recovered within six minutes (Fig. S18). Self-recovery has previously been reported for several mechanochromic compounds. 7,21 Grinding 1R at −25 °C afforded the transient green-emitting phase, and after 15 min, 1R was recovered (Fig. S18). On the other hand, the green-emitting phase obtained from 1R\textsubscript{Blue} at −50 °C remained intact for more than one day. These observations imply that the relative thermodynamic stability between 1R and 1G depends on temperature changes, which is the key to understand the mechanism underlying the low-temperature-selective mechanochromic properties of 1.

Based on the aforementioned results, we would like to propose a plausible mechanism for the mechano-induced phase transition of 1 (Fig. 5). To understand the mechanism of the low-temperature-selective mechanochromism of 1, the following three experimental results should be summarized: i) thermal phase transitions to afford 1G do not occur; ii) the phase transition from 1R/1R\textsubscript{Blue} to 1G can be induced mechanically; iii) the spontaneous phase transition to recover 1R from mechanically-processed 1G occurs in a certain temperature range. Based on these results, we propose a mechanism (Fig. 5), wherein the Gibbs free energy of 1R and 1G change depending on the temperature. At room temperature (Fig. 5a), 1R should be thermodynamically more stable than 1G. Judging from the transient behavior of the mechanochromism between −25 °C and 0 °C (Fig. S18), mechanical stimulation of 1R at room temperature should also induce a similar phase transition into 1G as at low temperature. However, 1G is immediately transformed into 1R, and the mechanochromism of 1 near room temperature is thus hardly detectable (Fig. S18). This should be caused by the higher Gibbs free energy of 1G and the low activation energy for the recovery of 1R at room temperature. Upon decreasing the temperature, the relative thermodynamic stability of 1R and 1G should change substantially (Fig. 5b); the decrease in free energy for 1G upon cooling should be greater than that of 1R and 1R\textsubscript{Blue}, probably due to the contribution of the entropy factor of 1G, which is larger than that of 1R and 1R\textsubscript{Blue}. Therefore, 1G, which is obtained by mechanical stimulation at this temperature, should exhibit a relatively high activation energy for the recovery phase transition into 1R (Fig. 5b). Further decreased temperatures should allow the ground phase to persist longer. Upon cooling 1 below −50 °C, unground phase 1R\textsubscript{Blue} should become thermodynamically less stable than 1G (Fig. 5c). Upon grinding below −50 °C, the mechano-induced phase transition from 1R\textsubscript{Blue} to 1G occurs.
The resulting 1G phase requires a high activation energy for the recovery phase transition to 1R, which should be unattainable at this temperature. Thus, the formation of a low-lying energy level of 1G at low temperature, which is too unstable close to room temperature, is the key to the mechanochromism of 1.

Fig. 5 Schematic representation of the temperature-dependent relative thermodynamic stability of 1R, 1R_{blue}, and 1G.

Conclusions

Herein, we report the unprecedented mechanochromism of 1, which can be detected exclusively at low temperature (<−50 °C). The red emission of 1R remains seemingly intact upon grinding at ambient temperature. Upon cooling, the emission color changes to blue (1R_{blue}) in the absence of a phase transition. Grinding of 1R_{blue} below −50 °C induces a prominent emission-color change from blue to green due to the formation of a new phase (1G). Single-crystal and powder XRD measurements indicated that the mechano-induced emission-color change at low temperature is caused by crystalline structure changes. Therefore, we suggest that the mechanism includes changes in the relative thermodynamic stability and activation energy for the recovery phase transitions. This study exemplifies the importance of a careful evaluation of the temperature-dependence of mechanochromic properties, which may result in the identification of novel phases that cannot be obtained by simple mechanical stimulation or thermal treatment.

Notes and references

12. In contrast to the solid state, monomeric 1 only shows weak photoluminescence in solution (Fig. S1).
13. To prevent the formation of ice on 1, we prepared a plastic bag filled with nitrogen gas, into which 1R, a heating/cooling stage, and a spatula were placed. After the heating/cooling stage was cooled to <−50 °C, we applied mechanical stimulation to 1R_{blue} with a spatula to afford 1G (Fig. S5). Under these conditions, even single, gentle scratches on the surface of the sample induced clear emission-color changes from blue to green at the scratched areas. After repeated scratching or grinding for approximately five minutes, almost the entire sample exhibited a green emission. However, an emission color change of the entire sample cannot be achieved by scratching. The resulting green-emissive part within the unaffected phase persists for several hours at <−50 °C. Under air, mechanochromism of 1 at low temperature was also observed.
14. We confirmed that the transformations between 1R, 1R_{blue}, and 1G are fully reversible for at least 30 cycles.
16. The emission spectrum of this single crystal at −150 °C is similar to that of the powdered form of 1R_{blue} (Fig. S10).
17. Patternless DSC profiles support the proposed absence of phase transitions between 1R and 1R_{blue} (Fig. S12).
18. The powder XRD pattern of 1R_{blue} agrees well with the simulated powder XRD pattern of the blue-emitting single crystal measured at −150 °C (Fig. S15).
19. For the powder XRD measurements, 1G was prepared by mechanical stimulation with a stirring bar in a test tube. For more details on the procedure and photographs, see Fig. S16.