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A meta-diisocyanide benzene-based aryl gold isocyanide complex exhibiting multiple solid-state molecular arrangements and luminescent mechanochromism

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Functional organic solids with switchable photoluminescence properties in response to external stimulation have attracted much interest because of their potential applications in sensors and imaging devices. Among these organic solids, luminescent mechanochromic compounds are emerging materials that can switch their photoluminescence properties when mechanically perturbed. Our group has intensively studied the solid-state emission properties and luminescent mechanochromism of a series of aryl gold isocyanide complexes. Here, we prepared bent-shaped binuclear gold isocyanide complex **2** that exhibits different pseudopolymorphs with different emission properties when prepared by different crystallization procedures. X-ray diffraction measurements and NMR spectroscopy identified inclusion of solvent molecules in the crystalline lattices of **2** except for one polymorph. Complex **2** also shows luminescent mechanochromism based on a crystalline-to-amorphous phase transition. The ground phases of all of the pseudopolymorphs revert to the polymorph without solvent molecules upon thermal treatment.

Introduction

Solid-state organic materials with tunable photoluminescence properties upon applying external stimulation have received recent attention owing to their potential applications in sensing and recording devices.¹ In these materials, the change of the emission properties by applying an external stimulus usually relies on a change in the assembly state of the chromophores in the bulk. This enables a change in the intermolecular interaction pattern, which often affects the electronic state of the material.² Incorporation of small molecules or solvent molecules is also effective to realize a new solid state of chromophores that differs from its exclusive assemblies.³ In this case, release of small molecules or solvent molecules from the bulk in response to external stimulation is the key for tuning the emission properties.^{3c-e}

Among the tunable emissive materials, luminescent mechanochromic compounds, which show an emission color change by mechanical stimulation, are an emerging class of functional materials.⁴ In 2008, our group reported the first example of reversible luminescent mechanochromism for the aryl binuclear gold isocyanide complex **1** (Fig. 1).⁵ This complex shows an emission color change from blue to yellow in response to mechanical perturbation, and the original blue-emitting

phase is recovered upon addition of dichloromethane (DCM) to the yellow-emitting ground powder. Besides the blue-emitting crystalline and yellow-emitting amorphous phases of **1**, no other solid states or solvent inclusion solids have been identified.⁶ Various organic and organometallic compounds with luminescent mechanochromic properties have subsequently been reported.⁷ Our group also reported related gold isocyanide complexes that show intriguing luminescent mechanochromism⁸ and related stimuli-responsivity.^{3c,9}

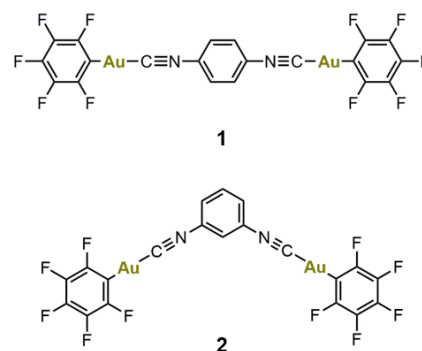


Fig. 1 Structures of **1** and **2**.

Here, we reported complex **2** (Fig. 1), the meta-substituted analogue of **1**. X-ray diffraction (XRD) measurements revealed that complex **2** forms multiple molecular arrangements containing solvent molecules depending on the crystallization procedure. Emission spectroscopy indicates that the various solid structures of **2** show distinct emission properties under ultraviolet (UV) light. All of the solid-state structures of **2** exhibit prominent luminescent mechanochromism based on

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crystalline-to-amorphous phase transitions. The resulting ground powder shows a reverse phase transition upon thermal treatment to give one polymorph of **2** with emission color changes.

Results and Discussion

Formation of pseudopolymorphic single crystals

We prepared compound **2** by the procedure reported for preparation of the para-substituted analogue **1**.⁵ The compound was characterized by ¹H NMR and high-resolution mass spectroscopy (see the ESI). Recrystallization of complex **2** from ethyl acetate (EA) and tetrahydrofuran (THF) gave three types of crystals with different shapes and emission spectra. When a solution of **2** in EA on an open Petri dish was evaporated for a week at 4 °C, block-shaped crystals **2a** were obtained (Fig. 2, left). A solution of **2** in THF gave two different single crystals: evaporation of the solution for 7 days at 4 °C gave needle-shaped crystals (**2b**, Fig. 2, left) and evaporation at 80 °C for 15 min gave rectangular crystals (**2c**, Fig. 2, left). Although **2a–2c** show green emission under UV illumination (Fig. 2, left), their emission spectra recorded under UV light are slightly different (Fig. 2, right). All of the emission spectra are broad and the emission peaks are located at 488 (**2a**), 495 (**2b**), and 519 nm (**2c**). A dilute solution of **2** in DCM has an emission spectrum with a peak at 414 nm (Fig. S1), indicating that the intermolecular interactions are important for the emission properties of the solid states. Expression of different emission properties of the solid states of a single compound indicates formation of distinct crystalline structures.¹⁰

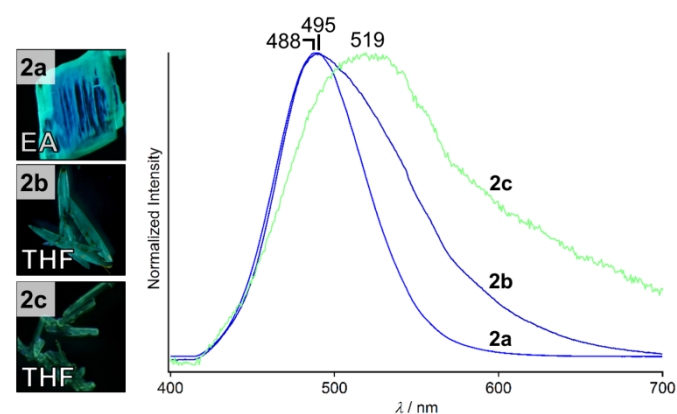


Fig. 2 Photographs (taken under UV light) and emission spectra (excitation at 365 nm) of **2a**, **2b**, and **2c**.

To obtain structural information about **2a–2c**, single-crystal XRD measurements were performed. **2a–2c** were of sufficient quality for single-crystal XRD, and the crystallographic parameters are given in Tables 1 and S1. As expected, the crystal structures of **2a–2c** are different even though **2b** and **2c** were crystallized using the same solvent (THF). Remarkably, these single crystals contain solvent molecules used for recrystallization, suggesting that **2a–2c** are pseudopolymorphs

of **2**. The single crystal of **2a** contains 2.5 equiv EA, whereas **2b** and **2c** contain 2 and 1 equiv THF, respectively (Tables 1 and S1).

Table 1 Crystallographic parameters of **2a**, **2b**, and **2c**.

	2a	2b	2c
CCDC number	1820938	1820947	1822803
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>P</i> -1 (#2)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> -1 (#2)
Inclusion (equiv)	EA (2.5)	THF (2.0)	THF (1.0)
<i>a</i> / Å	10.5053(14)	8.4401(7)	10.5280(9)
<i>b</i> / Å	11.0003(18)	17.3470(13)	11.5191(11)
<i>c</i> / Å	14.675(2)	19.5954(15)	11.8538(11)
α / °	79.575(5)	90	70.006(2)
β / °	87.376(4)	98.181(2)	70.754(2)
γ / °	86.965(5)	90	67.223(3)
<i>V</i> / Å ³	1664.4(4)	2839.8(4)	1212.85(19)
<i>Z</i> value	2	4	2
<i>D</i> _{calc} / g·cm ⁻³	2.148	2.340	2.542
<i>R</i> ₁ ^a	0.0757	0.0623	0.0689
<i>wR</i> ₂ ^b	0.2389	0.1544	0.2219
GOF ^c	1.039	0.990	0.979

^aFor data with *I* > 2.00σ(*I*). ^bFor all reflection data. ^cGoodness of fit indicator.

2a has the triclinic *P*-1 space group and includes EA molecules (Figs. 3 and S2).¹¹ The complex in **2a** adopts a flat conformation, with dihedral angles ϑ between the C₆F₅- rings and -C₆H₄- rings of 2.0(6)° and 4.0(6)° (Fig. S2b). The two short intermolecular distances between Au atoms of 3.1106(10) Å indicate formation of aurophilic interactions^{4a,12} with two neighboring molecules, which leads to formation of open-ended zigzag oligomeric chains (see the ORTEP representation in Fig. 3a). This zigzag chain interacts with a neighboring chain through double F...F interactions with F...F distances of 2.743(15) Å (inset in Fig. 3a). The resulting two-fold zigzag chain (Fig. 3a) is isolated from the neighboring two-fold zigzag chains because a lot of EA molecules ([EA]/[**2**] = 2.5) are located between them. All of the **2** molecules in the zigzag chains are surrounded by three EA molecules through formation of multiple C-H...O interactions between the hydrogen atoms of isocyanide benzene and the oxygen atoms of EA with distances ranging from 2.1 to 2.7 Å (red dotted lines in Fig. 3b). It should be noted that careful inspection indicates that there are no π-π stacking interactions of aromatic units within the zigzag chains.

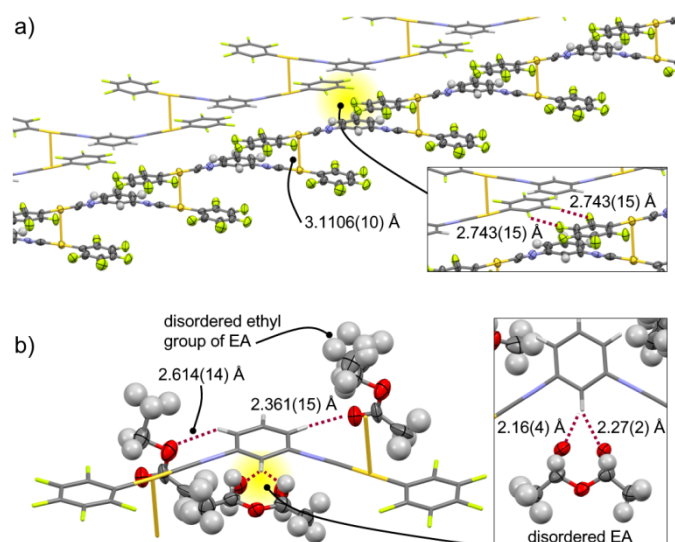


Fig. 3 Single-crystal structure of **2a**. (a) A two-fold zigzag chain containing intrachain aurophilic interactions and interchain double F...F interactions. (b) Three EA molecules (ORTEP representation) that surround one **2** molecule (stick representation).

Single-crystal structure analysis of **2b** indicates that it has the monoclinic $P2_1/n$ space group and includes THF molecules (Figs. 4 and S3). The **2** molecule has three aromatic rings: a meta-disubstituted C_6H_4 ring (ring A) and two C_6F_5 rings (rings B and C, Fig. 4a). The two dihedral angles are very different: $50.6(4)^\circ$ (between rings A and B) and $23.4(4)^\circ$ (between rings A and C), as shown in Fig. 4a. The B and C rings of the molecules form double Au... π interactions with the C and B rings of two neighboring molecules, respectively (highlighted in yellow in Fig. 4b). This gives an oligomeric zigzag chain (Fig. 4b). The zigzag chains are stacked through formation of π - π stacking interactions between ring A of one molecule and ring B of a neighboring molecule (Fig. S3b).¹³ As a result, an extended zigzag wall forms. The side and top views of the zigzag wall are shown in Fig. 4b and c, respectively. In this wall, the shortest distance between gold atoms is $3.7928(3)$ Å (Fig. S3c), indicating that there are no aurophilic interactions. The included THF molecules (space-filling representation in Fig. 4d) are located between the zigzag walls (the neighboring zigzag walls are colored green and magenta in Fig. 4d). The THF molecules form a one-dimensional (1D) channel through formation of several intermolecular interactions (Figs. 4e and S3d).

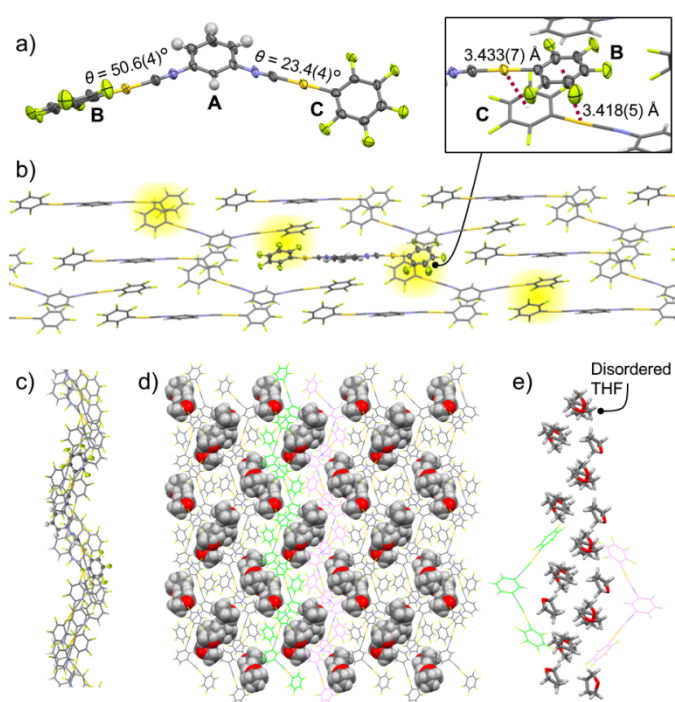


Fig. 4 Single-crystal structure of **2b**. (a) Monomer conformation of **2**. (b) Side and (c) top views of a zigzag wall containing intrachain double Au... π interactions. (d) THF molecules (space-filling representation) located between the zigzag walls. (e) THF molecules located in the 1D channel moieties.

Single-crystal XRD measurements of **2c** show that it has the triclinic $P\bar{1}$ space group and includes 1 equiv THF molecules (Figs. 5 and S4). In this crystal structure, the **2** molecules have a flat conformation with $\vartheta = 0.1(9)^\circ$ and $4.4(9)^\circ$ (Fig. S4b). These flat molecules form straight ribbon-like arrays of C_6F_5 -Au-CN- C_6H_4 - segments (see the ORTEP representation in Fig. 5a) through extended $(CF)_2\cdots H-C$ interactions with distances of $2.483(14)$ and $2.519(10)$ Å (red dotted lines in Fig. 5a). The straight ribbons have -NC-Au- C_6F_5 pendant segments at their periphery. THF molecules are located between these -NC-Au- C_6F_5 pendants and form O...H-C (distance $2.59(3)$ Å) and C...H...F-C interactions (distance $2.618(14)$ Å) with complex **2** (blue dotted lines in Fig. 5a). Thus, these THF molecules act as a glue to assist the ribbon-ribbon interactions within the flat sheets (Fig. 5a and b). Above and below each sheet, adjacent sheets (colored green and magenta, respectively, in the inset of Fig. 5c and in Fig. S4) are stacked with longitudinal offset. The **2** molecules in the middle sheet form two-fold aurophilic interactions (Au...Au distance $3.2859(13)$ Å) with the two neighboring complex molecules in the two adjacent sheets (Fig. 5c). Careful inspection indicates that there are no typical aromatic interactions (π - π and CH- π interactions) between the walls.

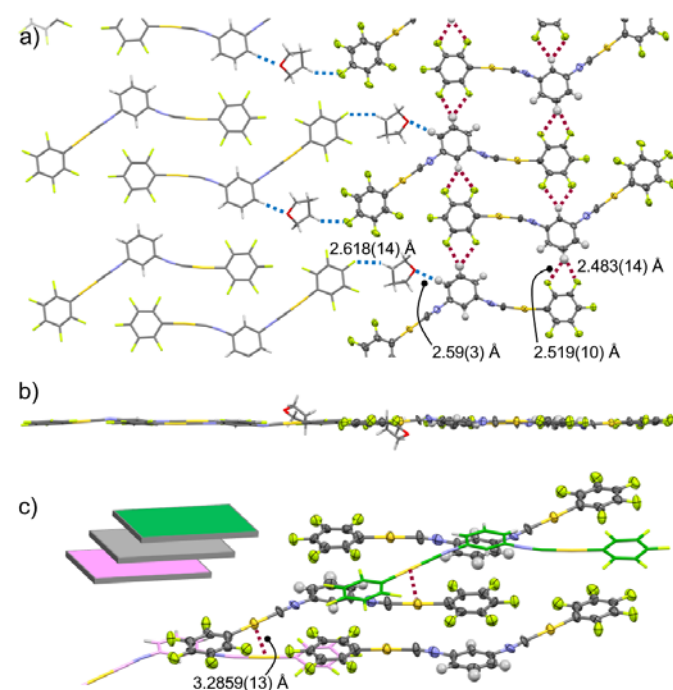


Fig. 5 Single-crystal structure of **2c**. (a) Top and (b) side views of a molecular sheet containing extended $(\text{CF}_3)_2\cdots\text{H}-\text{C}$ interactions of **2** (red dotted lines) and $\text{O}\cdots\text{H}-\text{C}$ and $\text{C}-\text{H}\cdots\text{F}-\text{C}$ interactions between **2** and THF (blue dotted lines). (c) Aurophilic interactions between molecular sheets. The inset shows a schematic representation of three stacked molecular sheets with longitudinal offset.

The results of crystal structure analysis of pseudopolymorphs **2a–2c** (solvent-included crystals) indicate the ability of **2** to form inclusion compounds and various molecular arrangements. This is in contrast to the previously reported para-substituted analogue **1**,⁵ in which no solvent inclusion is observed. In addition, rapid evaporation procedures give other crystalline phases of **2** that differ from **2a–2c**, which will be discussed in the next section.

Crystalline phases with different emission properties

The crystallization process and the solvent could affect the crystalline structures and emission properties of **2**. Simple evaporation of suspensions/solutions of **2** in various solvents also gave solid samples that show different emission properties from those of **2a–2c**. For example, rotary evaporation of a suspension of **2** in MeOH gave semicrystalline sample **2d**, which shows blue photoluminescence (Fig. 6, left). When the same procedure was used for homogeneous solutions of **2** in Et_2O , EA, and THF (see the ESI for the details), three distinct powdered crystalline samples of **2** were obtained, which are called **2e**, **2f**, and **2g**, respectively (Fig. 6, left).¹⁴ The emission lifetime measurements of **2d–2g** indicate that their average emission lifetimes are range of 0.8–5.0 μs , indicating phosphorescence (Fig. S6 and Table S2). These semicrystalline powders all show greenish emission under UV light (Fig. 6). The four crystalline samples **2d–2g** exhibit similar broad photoluminescence spectra (Fig. 6, right). However, their maximum emission wavelengths range from 492 to 517 nm and the emission peaks

are slightly different (inset in Fig. 6). This indicates that these crystalline samples may have distinct crystal structures.

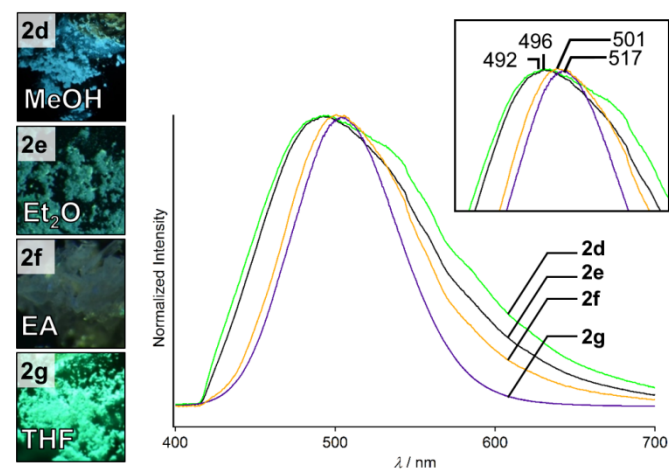


Fig. 6 Photographs of **2d–2g** taken under UV illumination. Emission spectra of **2d–2g** recorded under excitation at 365 nm.

Powder XRD analysis of **2d–2g** indicates that **2a–2g** are crystalline phases with different molecular arrangements. Repeated attempts to prepare single crystals of **2d–2g** failed, and thus powder XRD analysis was performed. Fig. 7 shows the experimentally obtained powder XRD patterns of **2d–2g**, which all exhibit intense diffraction peaks. Importantly, their peak positions and diffraction profiles are clearly different (Fig. 7). The diffraction patterns of **2d–2g** are also completely different from the simulated powder patterns of **2a–2c** derived from their single-crystal structures (Fig. 7). This indicates that the molecular arrangements of the seven crystalline samples **2a–2g** are different. This is in agreement with emission spectroscopy of **2a–2g** (Fig. S7), where the emission spectra have different emission maxima. After drying in vacuum for ~ 2 h, we measured the NMR spectra of **2d–2f** in acetone- d_6 (Fig. S8). The NMR spectra of **2e**, **2f**, and **2g** exhibit the proton signals of the solvent molecules used for crystallization (Et_2O , EA, and THF, respectively). These results indicate that the solvent molecules used for preparation are included inside the crystalline lattices of **2e–2f**, similar to **2a–2c**. In contrast, the proton signals of any solvent are not present in the NMR spectrum of **2d** (Fig. S8), indicating that there is no inclusion of the solvent.¹⁵

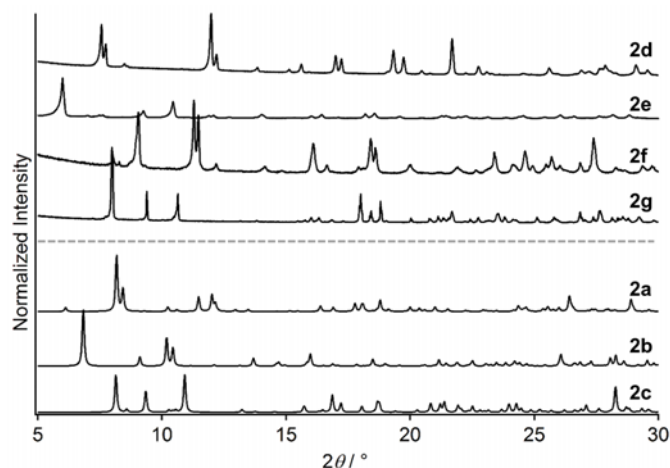


Fig. 7 Experimentally obtained powder XRD patterns of **2d–2g**. Simulated powder XRD patterns of **2a–2c** derived from their single-crystal structures

Luminescent mechanochromism

Upon grinding the seven solid states **2a–2g**, prominent luminescent mechanochromism with red-shifted emission is observed. For example, the blue emission of **2d** transformed to bright green emission upon mechanical stimulation on a glass plate (inset in Fig. 8a). The resulting powder sample **2_{ground}** shows a broad emission spectrum with a peak at 540 nm (Fig. 8a), which red-shifted by 48 nm upon grinding. The powder XRD pattern of **2_{ground}** shows a featureless profile after mechanical stimulation (Fig. 8b). Moreover, NMR spectroscopy and thermogravimetric analysis (TGA) confirm that no solvent molecules exist in **2_{ground}** (Figs. S10 and S11). These results indicate that the crystalline-to-amorphous phase transition^{8c,d} is the underlying mechanism for the luminescent mechanochromism of **2**. The ground powders obtained by grinding the other solid samples (i.e., **2a–2c** and **2e–2g**) show emission spectra similar to that of **2_{ground}** obtained from **2d** (Fig. S12). This indicates that all of the ground samples are the same irrespective of the solid phase of the unground form before mechanical stimulation.

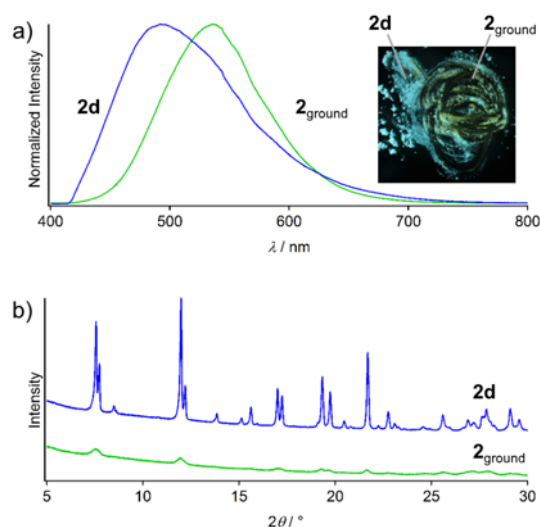


Fig. 8 (a) Emission spectra and photographs (under UV light, inset) of **2d** and **2_{ground}**. (b) Powder XRD patterns of **2d** and **2_{ground}**.

Upon heating the **2_{ground}** sample, a thermal phase transition occurs to give **2d** (the solvent-free polymorph obtained by crystallization with MeOH). When **2_{ground}** was heated on a glass plate under air, a gradual emission color change occurred at around 120 °C, and the emission color did not change upon cooling to room temperature (Fig. S13). The resulting powder sample has a similar emission spectrum to **2d** (Fig. S13). The powder XRD pattern of the heated sample contains intense peaks (Fig. S13), indicating recovery of the crystallinity upon increasing the temperature. This heated sample again shows luminescent mechanochromism in response to mechanical stimulation to give **2_{ground}** with intense green emission (Fig. S13). This result shows the reversibility of the phase transitions of **2** through mechanical stimulation and temperature control.

Conclusion

We have reported formation of multiple molecular arrangements of bent gold complex **2** that show various emission colors. Complex **2** can form various solid structures through specific crystallization procedures. For example, recrystallization of **2** from EA and THF gives three distinct single crystals **2a–2c**, which contain crystallized solvent. In addition to slow crystallization which gives **2a–2c**, rapid evaporation of solutions/suspensions of **2** in MeOH, Et₂O, EA, and THF gives **2d–2g**. Powder XRD analysis indicates that **2a–2g** all have different crystal structures and emission properties. Clear emission color changes are observed when **2a–2g** are mechanically stimulated. Upon heating the ground powders of all of the structures, the structure reverts to solvent-free **2d**, demonstrating the reversibility of the phase transition of **2**. Formation of multiple pseudopolymorphs of **2** is in contrast to **1**. This may originate from the bent molecular structure of **2**, which is ideal for creating room for solvent molecule inclusion upon packing. This results in formation of multiple molecular arrangements depending on the solvent. The insight obtained in this study can be used for preparation of solid materials that include small molecules or solvent molecules.

Acknowledgements

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11. **2a** shows an emission color change when it is left under ambient conditions (Fig. S8a). Therefore, the **2a** crystals are derived from the solution of **2** in EA just before the various measurements (i.e., XRD and spectroscopic measurements).
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13. The distance between the centroids of the two planes is 3.665(7) Å.
14. Evaporation of a solution of **2** in DCM gave a yellow-emitting crystalline powder (Fig. S5). From the powder XRD pattern with a rather broad profile (data not shown), this yellow-emitting phase may be a mixture of various molecular arrangements. We confirmed luminescent mechanochromism of this yellow-emitting powder (Fig. S5).
15. TGA of **2d** also supports that there is no solvent inclusion (Fig. S9).