Title	Photoluminescent Ferroelastic Molecular Crystals
Author(s)	Seki, Tomohiro; Feng, Chi; Kashiya, Kentaro; Sakamoto, Shunichi; Takasaki, Yuichi; Sasaki, Toshiyuki; Takamizawa, Satoshi; Ito, Hajime
Citation	Angewandte chemie-international edition, 59(23), 8839-8843 https://doi.org/10.1002/anie.201914610
Issue Date	2020-06-02
Doc URL	http://hdl.handle.net/2115/81628
Rights	This is the peer reviewed version of the following article: T. Seki, C. Feng, K. Kashiya, S. Sakamoto, Y. Takasaki, T. Sasaki, S. Takamizawa, H. Ito, Angew. Chem. Int. Ed. 2020, 59, 8839, which has been published in final form at https://doi.org/10.1002/anie.201914610 . This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.
Type	article (author version)
File Information	Ferroelastic_Au-NHC_200205_2.pdf

[Instructions for use](#)

Photoluminescent Ferroelastic Molecular Crystals

Tomohiro Seki,^{[a]*} Chi Feng,^[a] Kentaro Kashiya,^[a] Shunichi Sakamoto,^[b] Yuichi Takasaki,^[b] Toshiyuki Sasaki,^[b] Satoshi Takamizawa,^{[b]*} and Hajime Ito^{[a,c]*}

Abstract: Recently, ferroelasticity has been reported for several types of molecular crystals, which show mechanical-stress-induced shape change under twinning and/or spontaneous formation of strain. Aiming to create materials that exhibit both ferroelasticity and light-emission characteristics, we discovered the first examples of ferroelastic luminescent organometallic crystals. Crystals of arylgold(I)(*N*-heterocyclic carbene)(NHC) complexes bend upon exposure to anisotropic mechanical stress. X-ray diffraction analyses and stress-strain measurements on these ferroelastic crystals confirmed typical ferroelastic behavior, mechanical twinning, and the spontaneous build-up of strain. A comparison with single-crystal structures of related gold-NHC complexes that do not show ferroelasticity shed light on the structural origins of the ferroelastic behavior.

Ferroelasticity refers to a group of ferroic properties in analogy to ferromagnetism and ferroelectricity.^[1] In contrast to other ferroic materials, ferroelastic materials change their crystal morphology and/or crystal structure and show intriguing mechanical properties upon exposure to mechanical stress. Ferroelastic crystals exhibit plastic bending upon loading shear stress onto a specific crystal plane. Typically, a daughter phase appears at the bending domain, whose relative atomic or molecular orientation changes without transformation into a different crystal structure, which is indicative of twinning. Hysteresis stress-strain curves under spontaneous build-up of strain during crystal bending is another typical behavior of ferroelastic crystals. These phenomena are well documented for inorganic materials.^[2] Conversely, only few examples of twinning deformation have been reported for organic molecular crystals.^[3] One advantage of the ferroelasticity of organic crystalline materials relative to conventional inorganic materials is a large bend angle and a small force required for the twinning deformation. Moreover, it should be possible to implement other functions such as photoluminescence in parallel to the ferroelasticity.

Recently, Takamizawa and co-workers have systematically developed organoferroelastic materials such as 5-chloro-2-nitroaniline,^[4] adipic acid,^[5] 4,4'-dicarboxydiphenyl ether,^[6] *trans*-1,4-cyclohexane-dicarboxylic acid,^[7] and 2-methyl-5-nitrobenzoic acid,^[8] which show organoferroelasticity under twinning and the spontaneous build-up of strain. These molecules exhibit relatively simple molecular structures,^[4–9] and although mechanical twinning deformation of metallocenes^[10] has been reported,^[11] these do not exhibit organometallic ferroelastic behavior.

To generate ferroelastic molecular crystals that show photoluminescence properties, we focused on gold complexes. Among various organometallic compounds, gold complexes have many attractive features, such as a relatively uncommon linear coordination geometry, high chemical stability in air, a high tendency to form polymorphs in the solid phase, and prominent solid-state phosphorescence properties.^[12] It is also well known that gold complexes show various responses toward mechanical stress in parallel to photoluminescence color changes, i.e., mechanochromic luminescence.^[13] Our group has intensively investigated crystalline materials of gold complexes that include isocyanide, phosphine, and *N*-heterocyclic (NHC) ligands. We have reported that these complexes often show good crystallinity, photoluminescence, and other novel stimuli-responsive properties.^[13b,d–h,14] Recently, we have shifted our focus on NHC gold complexes^[15,16] to design structurally simple molecular scaffolds common in previously reported ferroelastic compounds.^[4–9] To realize ferroelasticity in organometallic gold complexes, we prepared various structurally simple NHC gold complexes (**1–4**) and investigated their mechanical properties. We discovered that NHC gold complexes **1** and **3** exhibit ferroelastic properties and spontaneous build-up of strain, i.e., **1** and **3** constitute the first examples of organometallic ferroelastic luminescent crystals.

Figure 1. Chemical structures of **1–4** and photographs of bent crystals of **1** and **3**.

[a] Dr. T. Seki, Mr. C. Feng, Mr. K. Kashiya, and Prof. Dr. H. Ito
Division of Applied Chemistry and Frontier Chemistry Center,
Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido
060-8628, Japan

E-mail: seki@eng.hokudai.ac.jp; hajito@eng.hokudai.ac.jp

[b] Mr. S. Sakamoto, Dr. Y. Takasaki, Dr. T. Sasaki, Prof. Dr. S.
Takamizawa
Department of Materials System Science, Graduate School of
Nanobioscience, Yokohama City University, 22-2 Seto, Kanazawa-
ku, Yokohama, Kanagawa 236-0027, Japan

E-mail: staka@yokohama-cu.ac.jp

[c] Prof. Dr. H. Ito
Institute for Chemical Reaction Design and Discovery (WPI-
ICReDD), Hokkaido University, Sapporo, Hokkaido, 060-8628,
Japan

Herein, we report the first examples of ferroelastic organometallic gold complexes that contain NHC ligands. Among the structurally similar NHC gold complexes **1–4**, crystals of **1** and **3** exhibit ferroelastic behavior upon loading shear stress onto specific crystal planes, while those of **2** and **4** do not. Based on single-crystal X-ray diffraction (XRD) measurements, the origin of the presence/absence of the ferroelasticity of **1–4** will be discussed. Complexes **1** and **3** are the first ferroelastic compounds that also show persisting photoluminescence upon crystal bending.

We also investigated the mechanical properties of the crystals of these NHC complexes. The synthesis of **1–4** is described in detail in the Supporting Information.^[17] Single crystals of **1–4** were obtained from recrystallization from CH_2Cl_2 /hexane. Upon exposing single crystals of **1** and **3** to stress, both crystals show mechanical bending (Figure 2a,b). The bent shapes are retained upon unloading the stress, which confirms plastic bending. Repeated experiments indicated that the bending angle of the crystals of **1** is reproducibly 45° (Figures 2a and S1). Scanning electron microscopy (SEM) measurements on bent crystals of **1** confirmed a continuous clear surface at the boundaries between the bent and unbent moieties (Figures 2c and S2). The SEM images even showed a 45° bending for the local domain ($\sim 5\ \mu\text{m}$) of the bent crystal edge of **1** that appeared upon loading stress (Figure 2d), which suggests a high tendency for bending at this angle. For crystals of **3**, similar properties were observed with respect to crystal bending and twinning (Figures 2 and S1). The bending angle of **3** is reproducibly $\sim 33^\circ$, which was confirmed by optical microscopy (Figure 2b) and by SEM (Figure S3). On the other hand, crystals of **2** and **4** are brittle, i.e., they are not susceptible to bending and easily collapse upon loading with mechanical stress (Figure S4).

Figure 2. Photographic of a) **1** and b) **3** upon loading with mechanical stress. c,d) SEM images of the bent crystals of **1**.

Single-crystal XRD analyses of bent crystals of **1** indicate that the deformation is due to mechanical twinning.^[18] Complex **1** crystallizes in the $P-1$ space group at 20°C (Figure S5 and Table S1),^[19] and the unit cell contains only one crystallographically independent molecule. The two aromatic rings of **1** include a dihedral angle (θ) of $4.7(3)^\circ$ and this flat conformation allows a head-to-tail stacking arrangement along the a axis with a π -

stacking distance of $3.415\ \text{\AA}$ (Figure S6). XRD analyses of **1** with face indexing indicated that the twinning deformation occurs upon bending via formation of daughter phase α_1 from mother phase α_0 when pushing in the $(0-10)$ plane (Figure 3). The twinning interface was assigned at $(-100)_{\alpha_0} // (100)_{\alpha_1}$, i.e., perpendicular to the stacked column. This result indicates that the lattices of the mother and daughter phase are correlated to each other by a 180° rotation along the $[100]$ direction (gray arrows in Figure 3). Based on these crystallographic results, a bending angle between α_0 and α_1 of 42.9° can be predicted, which agrees well with the bending angle (45°) observed by optical microscopy (Figure 2a) and SEM (Figure 2c,d). In order to achieve the aforementioned continuous boundaries between the twinning phases upon bending the crystals, such molecular rotations ($\sim 19^\circ$; inset in Figure 3c) can be expected to occur under a concomitant displacement (movement) of the constituent molecules along the bending direction. In the present case, it is also feasible to assume that a slippage between π -stacked columns occurs under retention of the overall column structure.

Figure 3. Photographic image of the twinning deformation of **1** as well as its crystal face indices and packing arrangements. Gray arrows indicate the rotation axis.

The single-crystal structure analyses of the mechanically bent crystals of **3** also indicate that a twinning deformation occurs upon loading mechanical shear stress similar to **1**. The overall crystal structure of **3** at 20°C ^[19,20] is similar in part to that of **1**: the space group is $P2_1/n$; the molecules adopt a flat molecular conformation ($\theta = 2.2(5)^\circ$) and form π -stacked columns in a head-to-tail arrangement (Figures 4 and S7 as well as Table S1). Mechanical twinning was clearly confirmed by face-index experiments upon pushing along the $[001]$ direction. The interface of **3** between the α_0 and α_1 domains is $(10-1)_{\alpha_0} // (10-1)_{\alpha_1}$ and we found that the rotational axis is oriented along the $[001]$ direction (gray arrows and dot in Figure 4). The bending angle of the crystal at the interface calculated from the crystallographic data is 40.4° (Figure 4c), which is roughly consistent with the results obtained from optical microscopy and SEM (Figure S3).

Figure 4. Photographic image of the twinning deformation of **3** as well as its crystal face indices and packing arrangements. Gray arrows and dot indicate the rotational axis.

Subsequently, we investigated the stress-strain relationship in crystals of **1** and **3** upon mechanical bending. For that purpose, we used the experimental setup of our previous studies:^[4–9] one end of the crystal was immobilized with epoxy glue, and the shear force was loaded by a jig to the specific crystal face of the other end of the crystal. Crystals of **1** start to detect the stress almost immediately when the jig reaches the crystal surface (Figure 5a, i). For **1**, the α_1 domain started to grow at an applied stress of 0.61 MPa (Figure 5a, ii). Similar to previously reported ferroelastic crystals, the shear stress is relatively constant upon further applying the force during the expansion of the daughter phase α_1 . After unloading the stress, spontaneous build-up strain was observed (Figure 5a, c). Upon subsequent loading of force from the opposite direction, the reverse deformation was induced to recover the original phase α_0 (Figure 5a, iii, iv). Throughout this process, a critical stress of 0.49 MPa was estimated. Such hysteresis behavior and the build-up of spontaneous strain clearly indicate typical ferroelastic behavior for **1** (Supporting Movie 2). As expected, similar ferroelastic hysteresis loops for the formation of daughter phase α_1 were observed for single crystals of **3** with a forward and reverse critical stress of 0.21 and 0.13 MPa, respectively (Figure 5b, d and Supporting Movie 3).^[21] These critical stress values are relatively weak compared to those of other previously reported ferroelastic crystals.

Figure 5. Photographic images and stress-strain hysteresis loops for the ferroelastic bending of crystals of a, c) **1** and b, d) **3**. Displacement rates: 10 μm/s (**1**) and 1 μm/s (**3**).

A comparison of the crystal structures of **1–4** provided insight into the structural factors that determine the ferroelasticity of **1** and **3**. The single-crystal structure analyses of non-ferroelastic **2** and **4** revealed that their overall structures are similar to those of **1** and **3**, which includes a flat molecular conformation, the formation of π -stacked columns, and weak column-to-column interactions (Figures S12 and S13 as well as Table S2). Nevertheless, only **1** and **3** show ferroelasticity (*vide supra*). To allow major molecular rotations (**1**: ~19°; **3**: ~20°) in the dense solid environment upon ferroelastic bending, sufficient space is required between the molecules. For **2**, the ethyl groups should prevent the molecular rotation due to the steric repulsion between the ethyl groups within the neighboring molecular columns (highlighted in blue in Figures 6b). Such steric repulsion between columns is not observed in **1**, **3**, or **4** (Figures 6a and S14). Molecular packing that is resistant to mechanical stress would be another factor required to prevent a simple collapse of the crystals upon bending. This feature would be facilitated by effective overlapping of molecular stacks via a combination of dipole-dipole and π - π stacking interactions. However, molecules of **4** in the columnar arrangement show a rotational displacement by ~30° (Figure 6d), which should decrease the structural resistance of the crystals of **4** toward mechanical force compared to those of the other compounds. Different from molecular columns of **4**, those of **1**, **2**, and **3** do not show significant rotational displacements (< 5°; Figures 6c and S15). These insights into the structure-property relationship derived from a series of NHC gold complexes may be helpful to develop principles for the design of advanced ferroelastic organic crystal materials.

Figure 6. Single-crystal structures of a) **1**, b) **2**, c) **3**, and d) **4**.

Moreover, crystals of **1** and **3** exhibit blue photoluminescence. Under exposure to UV light, crystals of **1** show a featureless emission spectrum with a maximum at 431 nm, a large absolute emission quantum yield ($\Phi_{\text{em}} = 0.65$), and phosphorescence character (average emission lifetime, $\tau_{\text{av}} = 0.43 \mu\text{s}$; Figures 7 and S16 as well as Table S3). A similar emission spectrum was observed for crystals of **3** ($\lambda_{\text{em,max}} = 452 \text{ nm}$; $\Phi_{\text{em}} = 0.42$; $\tau_{\text{av}} = 0.31 \mu\text{s}$) (Figure S17).^[22] We next investigated the effect of bending on the photoluminescence properties. The bent moiety (α_1) of **1** shows an emission spectrum similar to that of the unbent (α_0) moiety (Figure 7). Similarly, the bent moiety of crystals of **3** provided an unchanged emission spectrum (Figure S17). These results confirm that the photoluminescence properties of the crystals of **1** and **3** are stable toward mechanical deformation. This seems reasonable given that the impact of the mechanical force does not induce deterioration of the packing arrangements and the crystal structures of the twinned α_0 and α_1 phases, which differ only with respect to their relative orientation.^[23]

Figure 7. Emission spectra of the unbent (α_0) and bent moiety (α_1) as well as photographic images of a crystal of **1**.

We also investigated the effect of photoexcitation on the mechanical properties of crystals of **1** and **3**. For that purpose, the stress-strain hysteresis loops of **1** and **3** were re-examined under illumination with UV light. The results indicate that excitation from UV light does not significantly affect the ferroelastic behavior: the hysteresis loops under exposure to UV light are virtually identical to those obtained under exposure to visible light (Figures S20 and S21).

In summary, we report the first examples of ferroelasticity in organometallic NHC complexes of Au(I) under spontaneous build-up of intrinsic strain. Upon loading the stress, crystals of **1** and **3** show reproducible bending by 45° and 35° , respectively. X-ray diffraction analyses indicate that mechanical twinning occurs, i.e., that the molecular orientations are changed in the bent moieties. Stress-strain curves of crystals of **1** and **3** indicate typical ferroelastic properties, including the build-up of spontaneous strain and hysteresis loops. A comparison of the crystal structures of **1–4** suggested that an elaborate balance between the effective formation of π -stacked columns and appropriate intermolecular interactions between the columns are required to generate the ferroelastic behavior. Further exploration of NHC-ligated Au(I) complexes for the development of related functional molecular crystals with desirable mechanical properties are currently in progress.

Acknowledgements

This work was financially supported by the 2016–2018 Strategic Research Promotion (SK2810) of Yokohama City University and JSPS KAKENHI grants JP17H06370, JP17H06368, JP17K19143, JP18H03907, JP19H02784, and JP19H04555. This work was also supported by the Institute for Chemical Reaction Design and Discovery (ICReDD), which was established by the World Premier International Research Initiative (WPI) of MEXT, Japan.

Keywords: ferroelasticity • gold complex • photoluminescence • mechanical property

- [1] M. Fiebig, T. Lottermoser, D. Meier, M. Trassin, *Nat. Rev. Mater.* **2016**, *1*, 16046.
- [2] (a) C. Wang, X. Ke, J. Wang, R. Liang, Z. Luo, Y. Tian, D. Yi, Q. Zhang, J. Wang, X. F. Han, G. Van Tendeloo, L. Q. Chen, C. W. Nan, R. Ramesh, J. Zhang, *Nat. Commun.* **2016**, *7*, 10636; (b) E. Strelcov, Q. Dong, T. Li, J. Chae, Y. Shao, Y. Deng, A. Gruverman, J. Huang, A. Centrone, *Sci. Adv.* **2017**, *3*, e1602165.
- [3] I. Suzuki, K. Okada, *Solid State Commun.* **1979**, *29*, 759–762.
- [4] S. H. HapesMir, Y. Takasaki, E. R. Engel, S. Takamizawa, *Angew. Chem., Int. Ed.* **2017**, *56*, 15882–15885.
- [5] S. H. Mir, Y. Takasaki, S. Takamizawa, *Phys. Chem. Chem. Phys.* **2018**, *20*, 4631–4635.
- [6] E. R. Engel, Y. Takasaki, S. H. Mir, S. Takamizawa, *R. Soc. Open Sci.* **2018**, *5*, 171146.
- [7] S. H. Mir, Y. Takasaki, E. R. Engel, S. Takamizawa, *CrystEngComm* **2018**, *20*, 3807–3811.
- [8] S. H. Mir, Y. Takasaki, E. R. Engel, S. Takamizawa, *RSC Adv.* **2018**, *8*, 21933–21936.
- [9] (a) S. Takamizawa, Y. Takasaki, *Chem. Sci.* **2016**, *7*, 1527–1534; (b) S. Takamizawa, Y. Takasaki, *Cryst. Growth Des.* **2019**, *19*, 1912–1920; (c) S.

- Sakamoto, T. Sasaki, A. Sato-Tomita, S. Takamizawa, *Angew. Chem., Int. Ed.* **2019**, *58*, 13722–13726.
- [10] Y. Miyamoto, S. Takamizawa, *Dalton Trans.* **2015**, *44*, 5688–5691.
- [11] In ref. 9: Although mechanical deformation of the metallocene crystals due to twinning was confirmed, the spontaneous build-up of strain required for ferroelasticity was not observed.
- [12] (a) P. Pyykkö, *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456; (b) V. W. Yam, E. C. Cheng, *Chem. Soc. Rev.* **2008**, *37*, 1806–1813; (c) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951.
- [13] (a) M. Osawa, I. Kawata, S. Igawa, M. Hoshino, T. Fukunaga, D. Hashizume, *Chem. -Eur. J.* **2010**, *16*, 12114–12126; (b) H. Ito, M. Muromoto, S. Kurenuma, S. Ishizaka, N. Kitamura, H. Sato, T. Seki, *Nat. Commun.* **2013**, *4*, 2009; (c) P. Baranyai, G. Marsi, C. Jobbagy, A. Domjan, L. Olah, A. Deak, *Dalton Trans.* **2015**, *44*, 13455–13459; (d) T. Seki, Y. Takamatsu, H. Ito, *J. Am. Chem. Soc.* **2016**, *138*, 6252–6260; (e) M. Jin, T. Seki, H. Ito, *J. Am. Chem. Soc.* **2017**, *139*, 7452–7455; (f) T. Seki, N. Tokodai, S. Omagari, T. Nakanishi, Y. Hasegawa, T. Iwasa, T. Taketsugu, H. Ito, *J. Am. Chem. Soc.* **2017**, *139*, 6514–6517; (g) M. Jin, T. Sumitani, H. Sato, T. Seki, H. Ito, *J. Am. Chem. Soc.* **2018**, *140*, 2875–2879; (h) T. Seki, T. Mashimo, H. Ito, *Chem. Sci.* **2019**, *10*, 4185–4191.
- [14] (a) T. Seki, K. Kashiyama, H. Ito, *Dalton Trans.* **2019**, *48*, 7105–7109; (b) M. Jin, T. S. Chung, T. Seki, H. Ito, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2017**, *139*, 18115–18121.
- [15] (a) Y. Chen, G. Cheng, K. Li, D. P. Shelar, W. Lu, C.-M. Che, *Chem. Sci.* **2014**, *5*, 1348–1353; (b) A. A. Penney, V. V. Sizov, E. V. Grachova, D. V. Krupenya, V. V. Gurzhiy, G. L. Starova, S. P. Tunik, *Inorg. Chem.* **2016**, *55*, 4720–4732.
- [16] (a) C. M. Crudden, J. H. Horton, I. I. Ebraldize, O. V. Zenkina, A. B. McLean, B. Drevniok, Z. She, H.-B. Kraatz, N. J. Mosey, T. Seki, E. C. Keske, J. D. Leake, A. Rousina-Webb, G. Wu, *Nat. Chem.* **2014**, *6*, 409–414; (b) M. R. Narouz, K. M. Osten, P. J. Unsworth, R. W. Y. Man, K. Salorinne, S. Takano, R. Tomihara, S. Kaappa, S. Malola, C. T. Dinh, J. D. Padmos, K. Ayoo, P. J. Garrett, M. Nambo, J. H. Horton, E. H. Sargent, H. Hakkinen, T. Tsukuda, C. M. Crudden, *Nat. Chem.* **2019**, *11*, 419–425.
- [17] A. Johnson, M. C. Gimeno, *Chem. Commun.* **2016**, *52*, 9664–9667.
- [18] The single-crystal XRD analyses of as-prepared crystals of **1** and **3** do not show twinning, which supports the notion that the twinning of the bent crystals of these complexes occurs upon mechanical bending.
- [19] The single-crystal XRD analyses at –20 °C are shown in Figures S6 (**1**) and S8 (**3**) as well as Table S1.
- [20] For **3**, slight changes of the crystal structure were observed upon cooling below 0 °C (Figure S7–S9). Even at –20 °C, mechanical crystal bending (bending angle: ~40°) is possible without breaking the crystals (Figure S10). We also confirmed that **3** can show “superelastic” behavior below –40 °C (Supporting Movie S1), which will be described in detail elsewhere. For “superelasticity” (organosuperelasticity), see: S. Takamizawa, Y. Miyamoto, *Angew. Chem., Int. Ed.* **2014**, *53*, 6970–6973.
- [21] A similar ferroelastic stress-strain response of **3** can be confirmed at –1 °C with coercive forward and reverse stress of 0.14 and –0.08 MPa, respectively (Figure S11).
- [22] The optical properties of **2** and **4** are shown in Figure S18.
- [23] Even upon thorough grinding, **1** and **3** do not show luminescent mechanochromism (Figure S19).

Entry for the Table of Contents

COMMUNICATION

The first example of emissive ferroelastic molecular crystals based on a gold complex is reported.

ferroelastic and emissive

Tomohiro Seki,^{[a]*} Chi Feng,^[a] Kentaro Kashiwama,^[a] Shunichi Sakamoto,^[b] Yuichi Takasaki,^[b] Toshiyuki Sasaki,^[b] Satoshi Takamizawa,^{[b]*} and Hajime Ito^{[a,c]*}

Page No. – Page No.

Photoluminescent Ferroelastic Molecular Crystals