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Takumi Yoshida

Mechanical stimulation and solid seeding trigger single-crystal-to-single-crystal molecular domino transformations

Ito, H.; Muromoto, M.; Kurenuma, S.; Ishizaka, S.; Kitamura, B.; Sato, H.; Seki, T.
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1. Introduction

1.1 Single-crystal-to-single-crystal (SCSC) transformations

- Recently, functional materials that can be manipulated by external perturbations (heat, light, pressure, or guest molecules) are attracting interest for their potential utility as switches and sensors.

→ **To understand the origin of transformations is necessary.**

- Especially, single-crystal-to-single-crystal (SCSC) transformations of functional materials induced by external perturbations are desirable because single-crystal X-ray diffraction analysis provides a molecular-level understanding of the phase transformations.

1.2 Previous work by authors[1] : Mechanical stimulus triggered transformation

- Mechanical stimulus (shearing, ball-milling or grinding) is one of the external perturbations that can alter the solid structure of the molecular crystals.
- They previously found that Au complex showed reversible mechanochromism induced by mechanical stimulus (***Figure 1***)

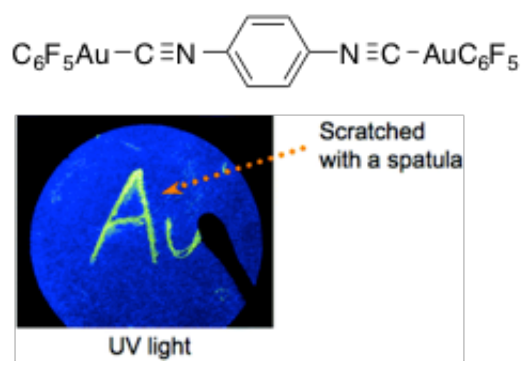

Figure 1. Structure of Au complex and photograph of mechanochromism

- After the mechanical stimulus (i.e. scratched with a spatula), strong mechanochromism was observed (blue→yellow).
- Treatment with dichloromethane leads to the original crystal (yellow→blue).

✗ They cannot analyze the resulting crystal after mechanical stimulus by single-crystal XRD analysis.

– Mechanical stimulus also induces crystal collapse, making them unsuitable for single-crystal X-ray analysis.

→ **Difficult to understand the mechanism of transformation induced by mechanical stimulus.**

1.3 This work

<u>Two novel points</u>

- The first observation of the SCSC transformation induced by mechanical stimulus.

→ **Mechanistic Consideration**

- The phase change first occurred at the initial contact area and subsequently progressed throughout the entire crystal.

→ **Behave as "molecular dominoes"**

2. Results and Discussion

2.1 Synthesis of Au Complex

- Au Complex **1** can be easily prepared (***figure*** 2).
- Rapid crystallization and slow crystallization from hexane/CH_2Cl_2 produced crystals of **1** in the $\mathbf{I_b}$ phase and $\mathbf{II_y}$ phase.

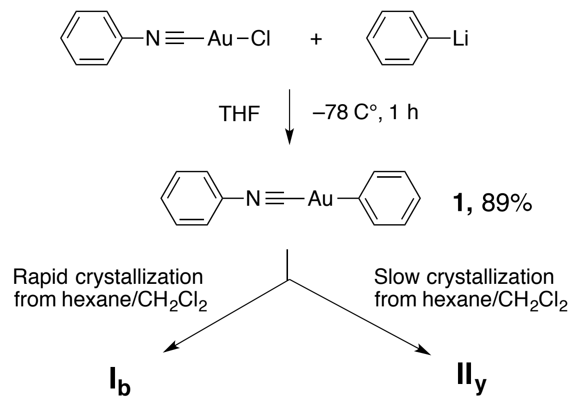

Figure 2. Preparation of Au complex

2.2 Properties of $\mathbf{I_b}$ and $\mathbf{II_y}$

- $\mathbf{I_b}$ showed blue photoluminescence
- $\mathbf{II_y}$ exhibited strong yellow photoluminescence (***figure 3***)
- X-ray analysis, elemental analysis, TG analysis and NMR measurement indicated that there was no solvent inclusion in the crystals.
- The crystal structures were confirmed by the single-crystal XRD analysis of each single crystals (***figure 4***)
- The big difference is the distance between the Au atoms.

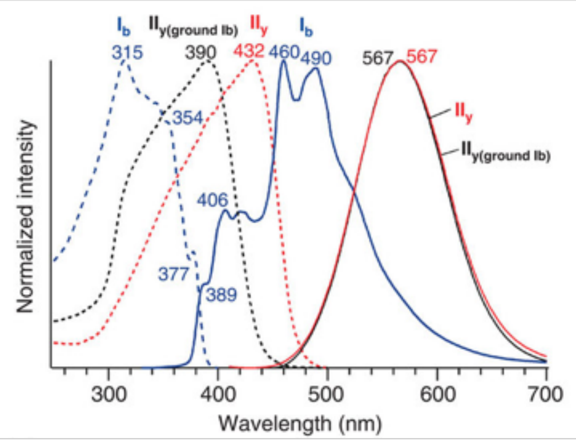

Figure 3. Emission and excitation spectrum of $\mathbf{I_b}$, $\mathbf{II_y}$ and $\mathbf{II_{y(ground\ Ib)}}$

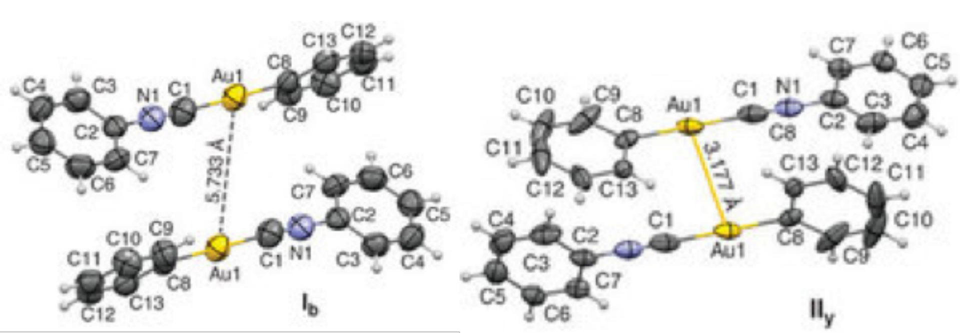

Figure 4. Crystal structure of $\mathbf{I_b}$ and $\mathbf{II_y}$

2.3 Mechanical stimulus for $\mathbf{I_b}$

- 3-min ball-milling of $\mathbf{I_b}$ afforded the powder $\mathbf{II_{y(ground\ Ib)}}$. It was identical to $\mathbf{II_y}$ in terms of its photoluminescence and XRD pattern.

→ These results indicate that the ball-milling process induced direct crystal-to-crystal transformation of $\mathbf{I_b}$ to $\mathbf{II_y}$

- Small pit was formed by using needle (***Figure 5***).
- Subsequently, the domain exhibiting yellow emission gradually increased to nearly the entire crystal after 9 h.

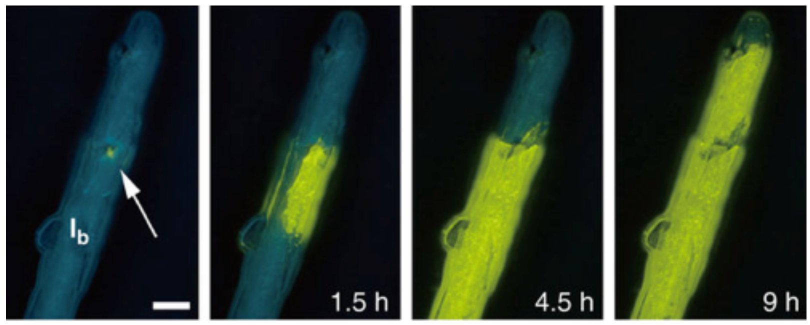

Figure 5. Photograph of SCSC transformation induced by mechanical stimulus

- The transformation was also triggered by contacting a seed crystal of $\mathbf{II_y}$ with a crystal of $\mathbf{I_b}$ (***figure 6***).
- The rate of conversion was highly variable.
- After the transformation, they got $\mathbf{II_{yscsc}}$ and single crystal X-ray analysis was performed.

→ The structure was identical to $\mathbf{II_y}$

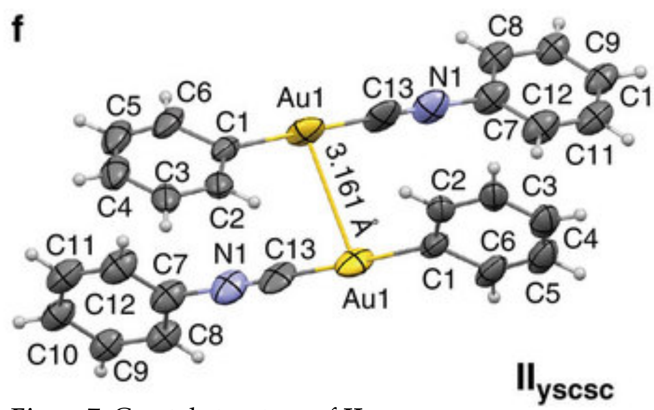

Figure 7. Crystal structure of $\mathbf{II_{yscsc}}$

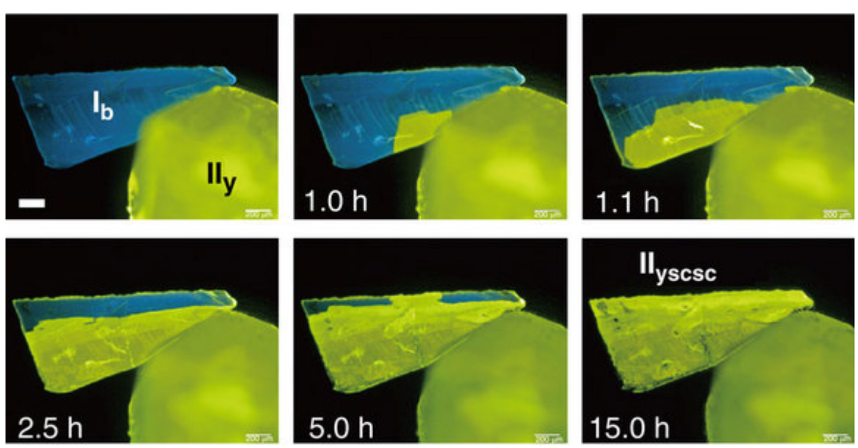

Figure 6. Photograph of Solid-Seeding SCSC transformation

2.4 Mechanism of SCSC transformation

- They considered the key of SCSC transformation is aurophilic interactions.
- Aurophilic interactions were generated within 3.5 Å[2]

→ It means that no aurophilic interactions in crystal $\mathbf{I_b}$ and existing aurophilic interactions in crystal $\mathbf{II_y}$.

- The result of DFT calculation shows that $\mathbf{II_y}$ shows shorter HOMO-LUMO gap compared to $\mathbf{I_b}$ (*figure* 7). This result is identical to red-shift emission spectrum.
- The less stable crystal $\mathbf{I_b}$ crystalizes first and more stable crystal $\mathbf{II_y}$ crystalizes from later (*figure* 8).

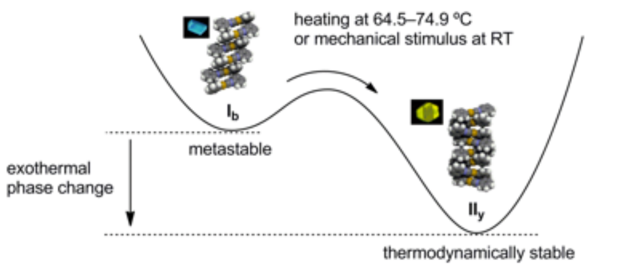

Figure 8. Diagram of the thermodynamic energies for $\mathbf{I_b}$ and $\mathbf{II_y}$

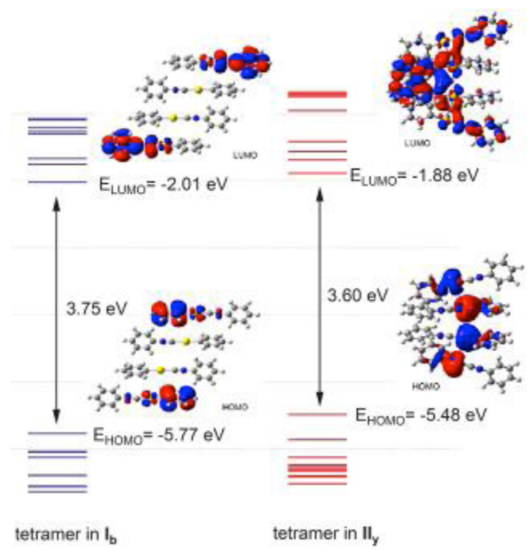

Figure 7. The result of DFT calculation

3. Conclusion

- First observation and single-crystal XRD analysis of SCSC transformation by mechanical stimulus.
- A mechanical stimulus triggers a state change in the entire assembly.

→It will be applied to highly sensitive detection of mechanical stimulation

4. Perspective

- Lack of reversibility (dissolution and recrystallization are necessary)

→Reversibility is suitable considering for the application

- We cannot design the complex to achieve this SCSC transformation.

→Only screening complexes

5. References

1) Ito, H.; Sato, T.; Oshima, N.; Kitamura, N.; Ishizaka, S.; Hinatsu, N.; Wakeshima, M.; Kato, M.; Tsuge, K.; Sawamura, M. *J. Am. Chem. Soc*. **2008**, *130*, 10044–10045.

2) Schmidhaur, H.; Schier, A. *Chem. Soc. Rev*. **2008**, *37*, 1931–1951.