

Design Amphiphilic Dipolar π -Systems for Stimuli-Responsive Luminescent Materials Using Metastable States

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1. Introduction

1-1. Background of Mechanochromism Materials

- Mechanochromism materials: luminescent materials responsive to mechanical stimuli.
- They have the ability to tune their molecular, physical, or chemical properties *via* macroscopic stimulation, which can be applied for sensors and imaging devices.
- Three major mechanistic explanations for color change upon aggregation :
 (1) excimer formation, (2) excimer dissolution, and (3) changes in chemical structure.
- However, development of these materials depends on *serendipitous discovery* or *random screening*.
 → Rational design for luminescent compounds with sensitivity to mechanical stimuli has not been reported to date.

1-2. This Work: molecular-level rational design of a new mechanochromic material

Introduction of *amphiphilic* and *dipolar characteristics* into luminescent π -conjugated molecule.

→ Several metastable forms that are sensitive to external stimuli.

2. Results and Discussion

2-1. Molecular Design (Figure 1)

- Molecule **1** has three characteristics.
- **Luminescence:** oligo(*p*-phenylenevinylene) (OPV)
- **Amphiphilicity:** hydrophobic **dodecyl chain** and hydrophilic **tri(ethylene glycol) (TEG) chain**
- **Dipole Moment:** an electron-donating **amino group** and an electron-withdrawing **ester group**
- Two different interactions (amphiphilic and dipolar interaction) result in several metastable aggregation forms and thus photoluminescence could be tuned.

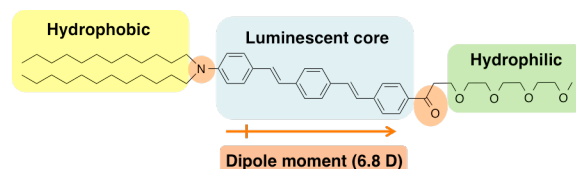


Figure 1. Chemical structure of compound **1**.

2-2. Photoluminescence change in various solvents (Figure 2)

- In solution, **1** exhibits a solvatochromic photoluminescence shift from blue to red as the polarity of solvent increases.
- This molecule has intramolecular charge-transfer ability.

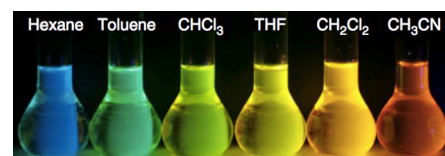


Figure 2. Solutions (10^{-5} M) of **1** in various solvents

2-3. Color change in four different aggregation forms (Figure 3)

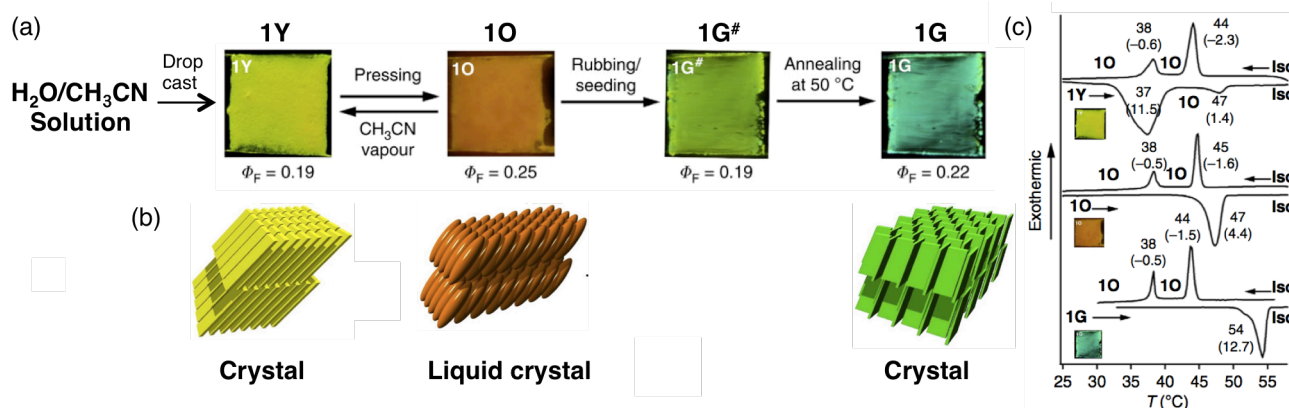


Figure 3. (a) Photographs of a thin film of **1** showing stimuli-responsive change in the luminescent under UV (365 nm) irradiation. (b) Schematic illustration of phase transition. (c) DSC traces with the phase-transition temperatures.

When the solution of **1** was drop-casted on a glass substrate, a thin film of **1** exhibited yellow photoluminescence (Formation of **1Y**).

- After pressing **1Y**, the luminescence color became orange (Formation of **1O**).
- After rubbing **1O**, the luminescence color became green (Formation of **1G[#]**).
- After annealing **1G[#]** at 50 °C, the luminescence color became bluish-green (Formation of **1G**).
- Differential scanning calorimetry (DSC) measurements (Figure 3c) revealed that all three phases became **1O** by cooling the isotropic phase to rt (**Iso**).

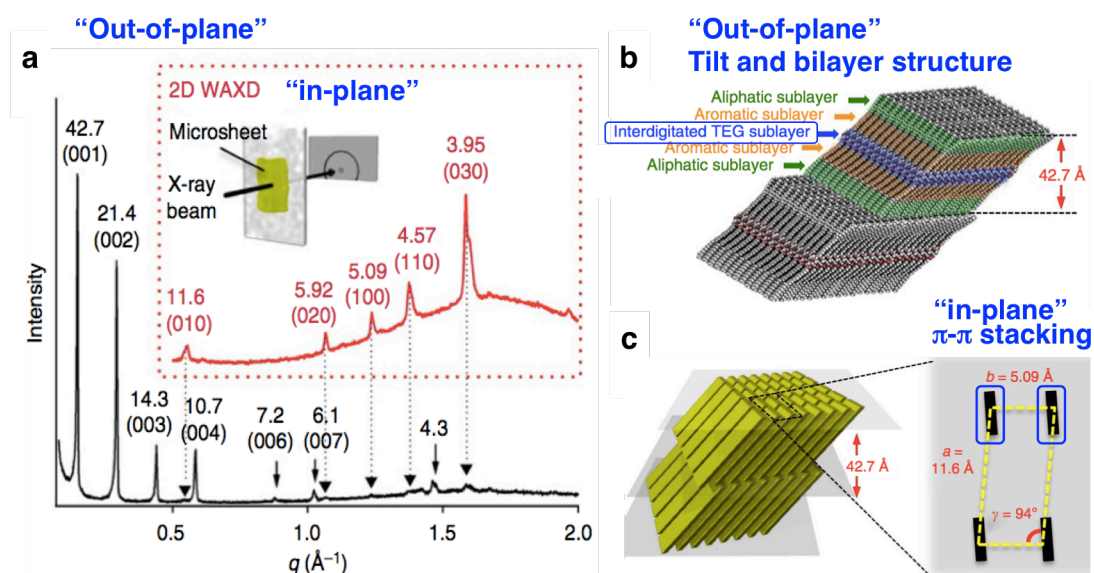
2-3-1. Structure of Yellow Phase (**1Y**) determined by Power X-ray diffraction (PXRD) analysis

Figure 4. (a) PXRD patterns of **1Y** with major *d*-spacings. (b) Schematic representation of layer structure of **1** in **1Y**. (c) Schematic illustration of in-plane packing of **1** in **1Y**.

- "Out of plane" reflections → Tilt and bilayer form with interdigitated TEG chains (Figure 4b)
- "In-plane" reflections → π - π stacked OPV moieties (Figure 4c)

- Solid-state absorption measurement of **1Y** revealed blue-shift compared to CH₃CN sol. (Figure 5).
→ **1Y** stacked into face-to-face (H-aggregate).
- This aggregation is driven by the segregation of hydrophobic and hydrophilic moieties.

2-3-2. Orange Phase (**1O**)

- PXRD analysis showed that the molecule **1** forms layer-by-layer structure and rotates in the molecular long axis. → Liquid crystal (Figure 6b)
- Photoluminescence of **2** is similar to that of **1O**.
- X-ray single crystal analysis of **2** clarified that OPV cores adopt three conformations; one ordered and two disordered conformations (Figure 6d).

“Why **1O** was red-shifted compared to **1Y**??”

- The two boat-like conformers exhibit a geometrical distortion. → The authors considered that this distortion is responsible for the long-wavelength emission.

➤ *In my opinion...*

- 1) Dipole was antiparallel → more stable than parallel
- 2) Twisted intramolecular charge transfer (TICT) occurred due to the freedom of the molecular geometry in liquid crystal state.

2-3-3. Green Phase (**1G** and **1G[#]**)

- PXRD analysis showed that the molecule **1** in **1G** form crystal state with a layer-by-layer structure (Figure 8a).
- Green emission from **1G** (Figure 5)
- → The luminophores are monomeric assembly and thus free of π - π stacking interactions (Figure 8b).
- Structure of **1G[#]** is similar to that of **1G**, but less crystalline form of **1G**.

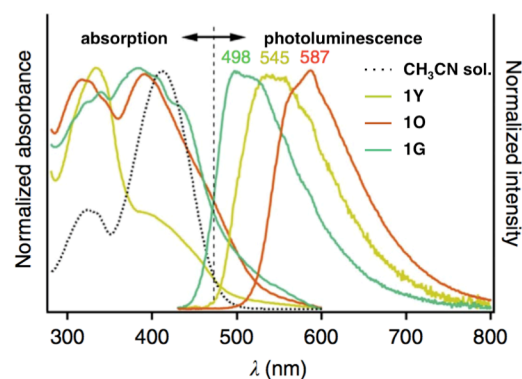


Figure 5. UV-Vis absorption and fluorescence spectra.

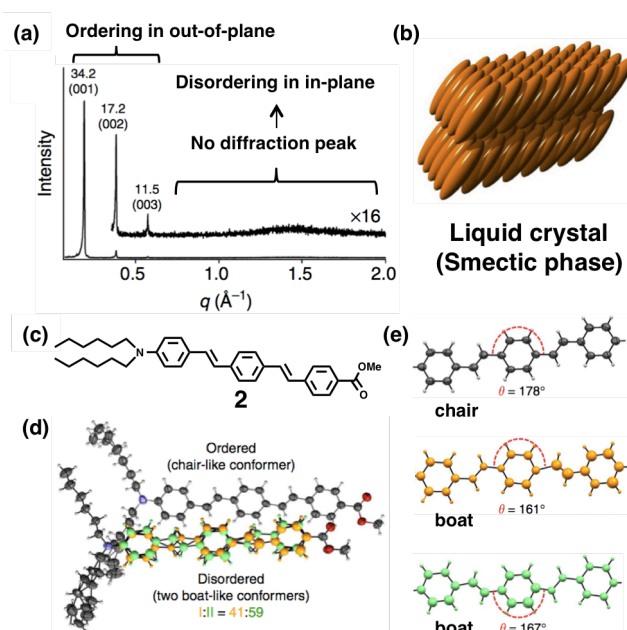


Figure 6. (a) PXRD of **1O**. (b) Schematic illustration of **1O**. (c) Chemical structure of **2**. (d,e) Single crystal structure of **2**.

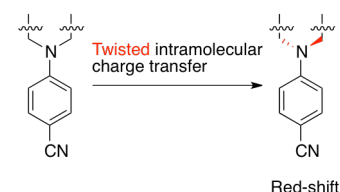


Figure 7. Schematic illustration of TICT emission.

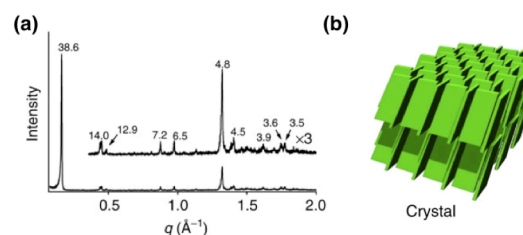


Figure 8. (a) PXRD of **1G**. (b) Schematic illustration of **1G**.

2-4. Controlling Crystallization Using a Lithium Salt

- Once an edge of **10** was rubbed (**1G[#]** seeded), **1G[#]** phase spontaneously developed toward the surrounding area at ~ 1.0 mm/h at rt (Figure 9).
- Thermal conversion (**1G[#]** \rightarrow iso \rightarrow **10**) occurred by soldering iron (Figure 10a).
- Without Li (upper half): **10** \rightarrow **1G[#]** (at rt, 1 h)
- Immersed into Li solution (lower half) : **10** remained (Figure 10b)

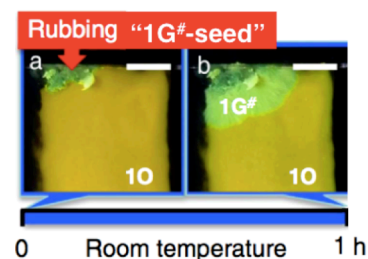


Figure 9. Spontaneous propagation of **1G[#]** on **10** under UV light.

- The chelation with the lithium salt canceled the molecular tilt owing to the loss of the interdigitation of the TEG moieties (Figure 10c).

Application of the lithium-responsive property to invisible inkjet printing (Figure 10d).

- A butanol solution of $\text{CF}_3\text{SO}_3\text{Li}$ (5 wt%) was dropped on thin films of **10** and painted invisible images *via* inkjet printing (Figure 10d).
- When small crystallites of **1G[#]** were seeded (rubbing) onto the **10** film, the picture of orange fruit and the characters “ORANGE” appeared (Figure 10e).

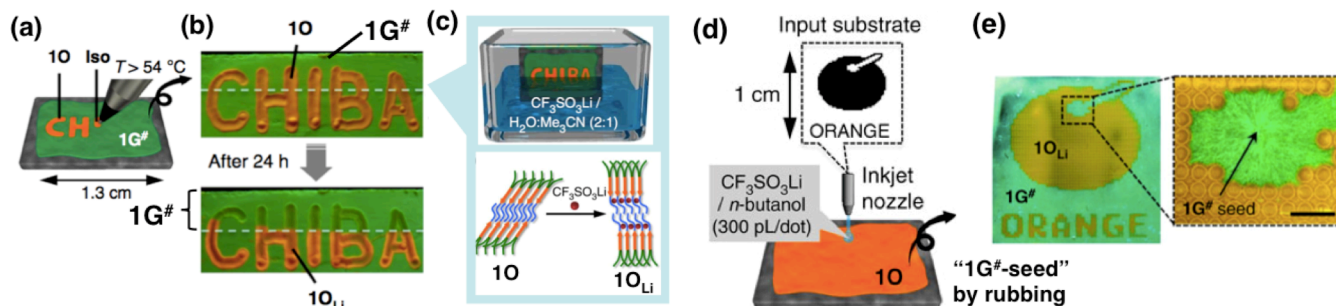


Figure 10. (a) Thermal writing using Iso (converted to **10** upon cooling) on **1G[#]**. (b) Photographs exhibiting the control over the auto-erasure of **10** on **1G[#]** under UV light. Only the lower half of the glass plate was immersed in an aqueous acetonitrile solution containing $\text{CF}_3\text{SO}_3\text{Li}$. (c) Schematic representation of orientational change of **1** upon complexing with the lithium salt (shown by red balls). (d) Inkjet writing of a cartoon picture of an orange fruit and the characters ‘ORANGE’ on **10** by using *n*-butanol solution of $\text{CF}_3\text{SO}_3\text{Li}$ (5 wt%). (e) Photograph of the inkjetted sample under UV light after **1G[#]** seeding. Inset shows the fluorescent microscopic image of a part of the orange picture (scale bar, 0.5 mm).

3. Conclusion

- The author designed mechanochromism materials, which contains dipolar and amphiphilic characteristics \rightarrow Driving force of transformation.
- The molecule can form four different aggregation states (**10**, **1Y**, **1G[#]**, and **1G**).
- They applied this molecule to invisible inkjet printing as a “molecular key”.

4. References

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- (2) 分子光化学の原理 Principles of Molecular photochemistry: An Introduction
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