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Solid-state luminescence of Au(I) complexes with external stimuli-responsive properties

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Abstract

In the last decade, the field of stimuli-responsive luminescent materials have been intensely emerged because of the high potential application to functional sensors or photoelectronic devices. In particular, luminescent molecular crystals constructed from Au(I) complexes have produced a wide range of examples of luminescent alterations when some external stimulations, such as heat, mechanical stress, vapor (or solvents), were applied to the solid samples. In this review, we describe the recent progress through a summary of the reported Au(I) complexes based on their utilized stimuli-responsive mechanisms, which are categorized in crystal phase transitions (“crystal-to-amorphous”, “crystal-to-crystal” and “single-crystal-to-single-crystal” transitions) and molecular rotation in crystalline media, respectively.

Keywords: Luminescent Au(I) complexes, External-stimuli-responsive solid-state emission, Crystalline phase transition, Crystalline molecular rotors

1. Introduction

Near the decade, solid-state luminescent molecular materials exhibiting photo-physical properties alterations by external stimulations, such as heat, vapor, photo, and mechanical stress, have attracted many interests because of their high potential to generate new functional sensors or security materials [1,2,3]. In general, the luminescent properties of solid samples are highly dominated by the electronic environment of luminophore in bulk space, and the property is deeply linked to intermolecular packing mode or molecular conformation [1]. Therefore, when luminophores in the assembly experience the change of packing environment during the stimulus, the excitation process could be altered, resulting in emission properties

alterations (Figure 1). However, it is still issued to control and create the phase transition of ordered assembled structures such as crystal. Furthermore, controlling the emission properties in the solid phase is also a difficult subject because no rational design strategy is available to control over inter or intramolecular structure of the luminophores in the solid phase. Additionally, the solid phase can easily experience some unexpected energy transfer, generally disturbing luminescence control, making the property control more difficult.

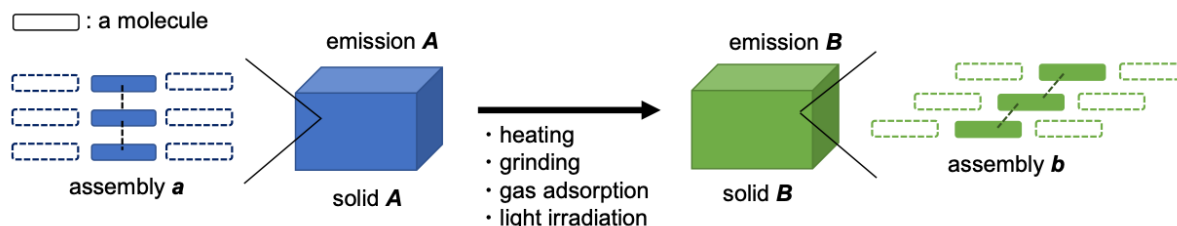


Figure 1. Representation of the external stimulation-responsive luminescence of solid-state molecular materials.

Organic molecules possessing large π -conjugated domain or organometallic compounds have been broadly developed as solid state luminophores, [1,2,3]. In particular, luminescent Au(I) complexes have been intensely reported as a promising compound for producing external-stimuli-responsive emission in aggregated media [4,5]. In general, luminescence properties of Au(I) complexes have originated from an electronic environment near the metal-centered domain. For example, a monomer of luminescent Au(I) complex possesses an aryl group as a ligand that can exhibit π - π^* transition and charge-transfer event between the d orbitals in the Au atom, which can produce a multiple excitation pathway and emission components (Figure 2a). Especially, the metal-to-ligand charge-transfer (MLCT) event during the excitation process is usually influenced by the geometry of the ligand because of its direct effect on the overlap of the contributed molecular orbitals of the Au(I) atom and the ligands. In addition, the Au(I) complexes can exhibit auophilic interactions when the Au(I) atoms take a close distance, below ca, 3.5 Å [4,5]. This geometry of Au(I) complexes results in destabilization of d_z^2 orbitals in the Au(I) atoms, forming $d_z^2\sigma^*$ orbital, and the newly formed $d_z^2\sigma^*$ orbital act as the HOMO (Figure 2b). As a result, the luminescence with auophilic interactions is displayed via metal-metal-to-ligand charge transfer (MMLCT), exhibiting phosphorescence and has a lower HOMO-LUMO energy gap inducing red-shifted absorption or emission spectra (Figure 2b). In addition, the auophilic interactions generally induce higher emission intensity. According to these features, the electronic environment and luminescence of Au(I) complexes can be influenced by internal or external changes, molecular conformations, the dipole moment of neighboring systems, and alternative molecular arrangements [4,5].

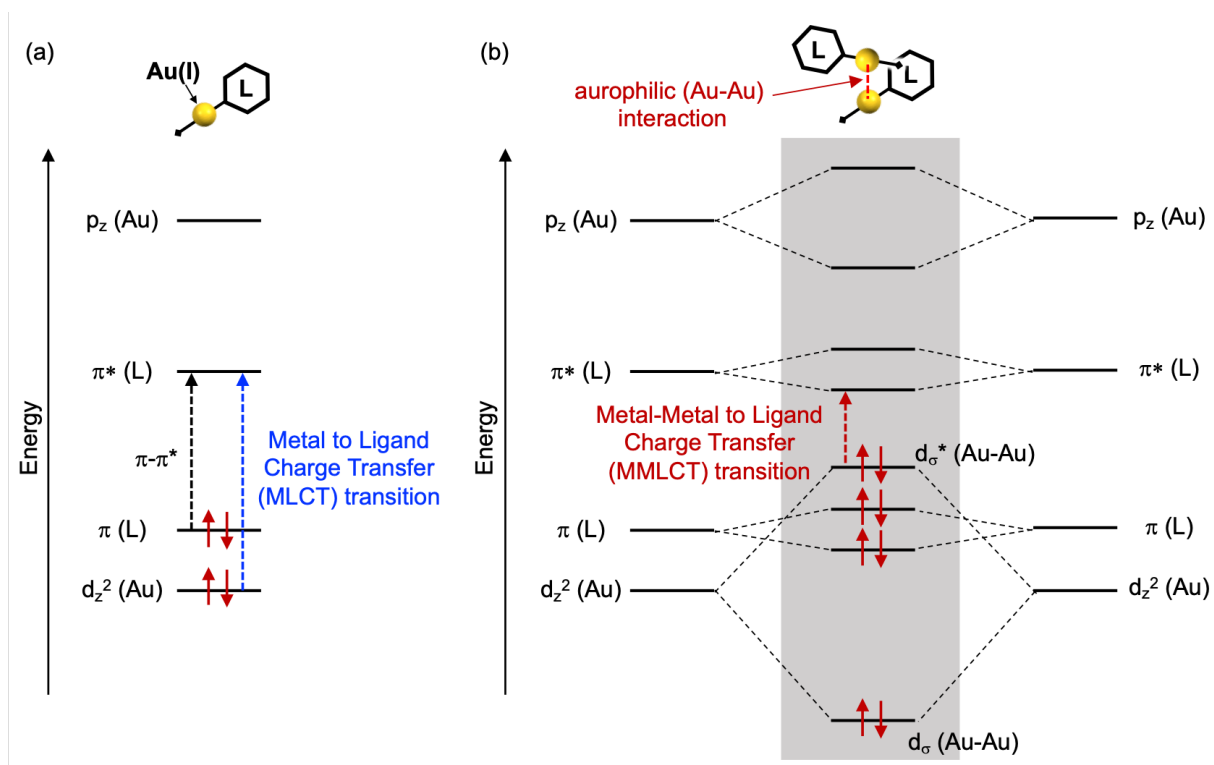


Figure 2. Schematic representation of molecular orbitals diagram of Au(I) complex in (a) monomer and (b) when forms intermolecular aurophilic interactions.

Molecular arrangement alterations of crystalline phase can be categorized into “crystal-to-amorphous,” “crystal-to-crystal,” and “single-crystal-to-single-crystal” phase transitions [1]. During crystal-to-amorphous transition, it occurs that a highly ordered molecular packing environment converts to a randomly arranged packing manner in solid-state (Figure 3a). Thus, a clear broadening in the X-ray diffraction (XRD) pattern is observed when the crystal-to-amorphous phase transition occur. However, detailed information of molecular structure and packing mode in the amorphous phase cannot be obtained, and it is difficult to understand the phenomena. In contrast, “crystal-to-crystalline powder” or “single-crystal-to-single-crystal” phase transition can convert the molecular arrangement with persisting of the phase order (Figure 3b). In this case, crystal structures of the initial and resulted phase can be given by single-crystal XRD measurements, allowing the understanding of molecular-level structural transition in the solid phase. It is still a challenging subject to design the solid-state phase transitions of molecular crystals because the prediction of intermolecular interactions as well as packing manner is very difficult. Much effort has been made towards the rational design of crystalline phase transitions, utilizing the “meta-stable” and “thermodynamically stable” phases. Generally, phase transition can occur from the meta-stable phase to the thermodynamically stable phase when external stimulations afford to overcome the activation

energy barrier (Figure 3c). There are several approaches to build the meta-stable phase via hybrid rigid and soft media in aggregated phase; however, it is still unclear as a solid concept for the rational design [1].

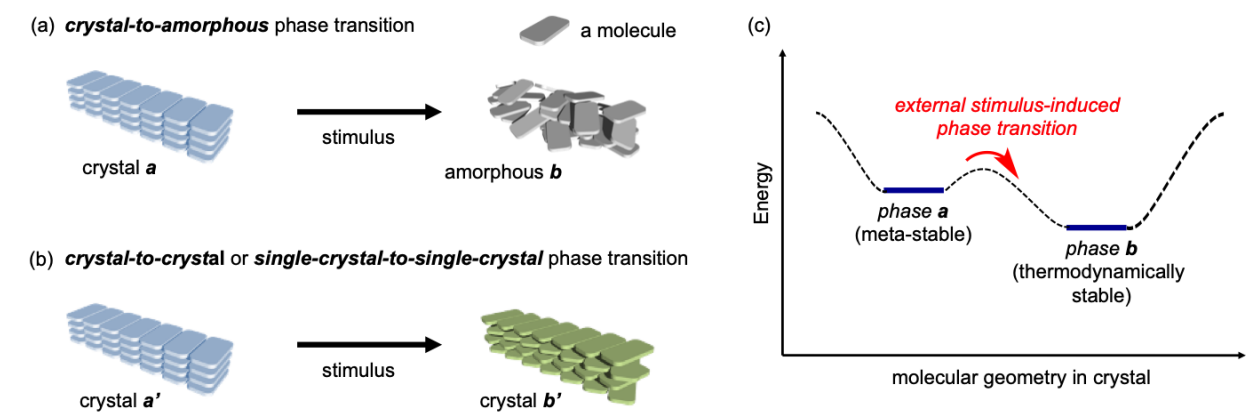


Figure 3. Series of crystal phase transitions via applying external stimulations. (a) crystal-to-amorphous transition and (b) crystal-to-crystal or single-crystal-to-single-crystal transition. (c) Schematic diagram for describing the relationship between “meta-stable” and “thermodynamically stable” phases with the inter-conversion by external stimulations.

Generally, molecules are forced to decrease their degrees of freedom in the crystals due to the close packing environment. More recently however, crystalline molecular rotors have emerged as a novel crystalline phase, which furnish high phase order and exhibit fast molecular rotation, defined as “amphidynamic crystal” by Garcia-Garibay (Figure 4a) [6,7,8,9]. As described in Figure 1a, the crystals, representing on the top right corner, can be constrained to specific lattice positions while other components exhibit rapid molecular motion. This newly investigated class of solid phase has been considered as providing many exciting opportunities in solid-state materials science. From single-crystal XRD, we can get accurate static structure information for amphidynamic crystals. However, there is no direct information for molecular dynamics in the crystal via the usual single-crystal XRD measurement. Thus, coupling of complementary techniques that span a much more comprehensive range of frequencies, such as several solid-state NMR measurements (CP-MAS, wide-line analysis of ^2H spin-echo, and T_1 spin-lattice relaxation) in variable temperature should be performed to the amplitude and frequency of motion, as well as the energy of activation of the dynamic process within the crystal lattice [6]. For constructing amphidynamic crystals, the components working as static frames to support the dynamic portions of the system should be needed. In addition, highly mobile components, defined as rotators, may have free volume around themselves within the crystal lattice [6,7]. The stator should connect to the rotators through suitable axles that support their rotary motion or through pivots that support an oscillatory movement. Based on this

idea, several molecular or material designs for constructing the amphidynamic crystals have been reported, such as macroscopic gyroscopes, metal-organic frameworks (MOFs), mesoporous organosilicas, organic cages, and porous aromatic frameworks (Figure 4b) [6,7,8,9].

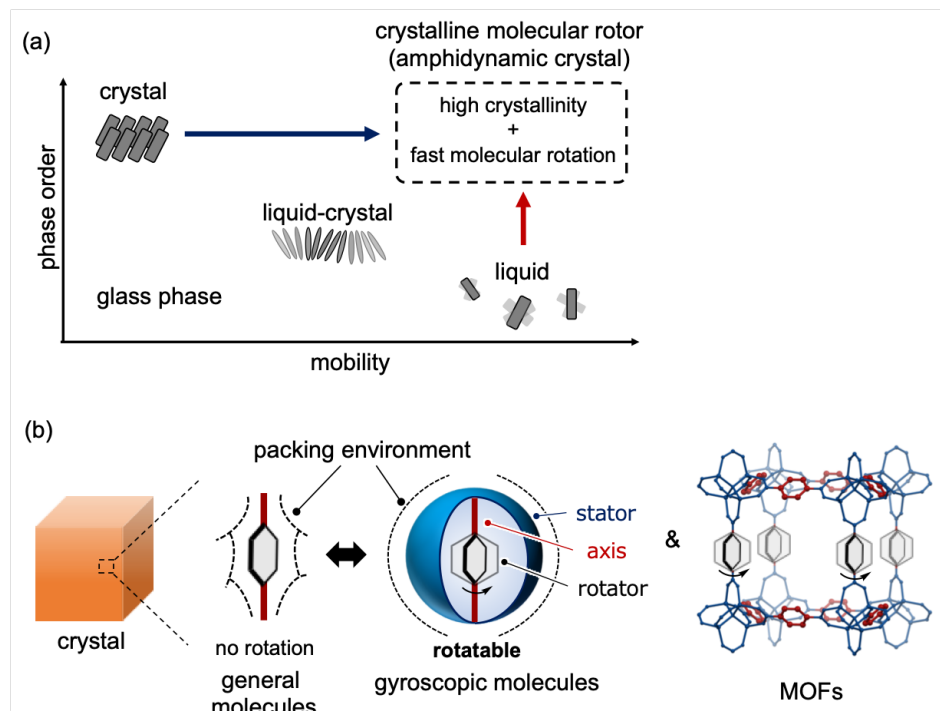


Figure 4. Amphidynamic crystals showing molecular rotation in the highly ordered phase. (a) A plot of phase order versus molecular mobility with a schematic representation of several assembly phases. (b) Molecular design concepts for constructing amphidynamic crystals

In this review, we will describe comprehensive advance in external stimuli-responsive molecular crystals via luminescent Au(I) complexes. Notably, the examples were categorized in two sections according to molecular arrangement alterations via crystal phase transitions (crystal-to-amorphous, crystal-to-crystal, or single-crystal-to-single-crystal transition manners) molecular conformation change via the rotational motion in amphidynamic crystals. Focusing on external stimulations, we discussed mechanical stress, solvent addition, temperature change, and photo-irradiation. Through the review, we noted that a combination of luminescent features of Au(I) complexes with crystalline phase transitions of molecular rotations in crystalline media had provided a conceptual motif to design the external stimuli-responsive luminescence in solid-state materials (Figure 5).

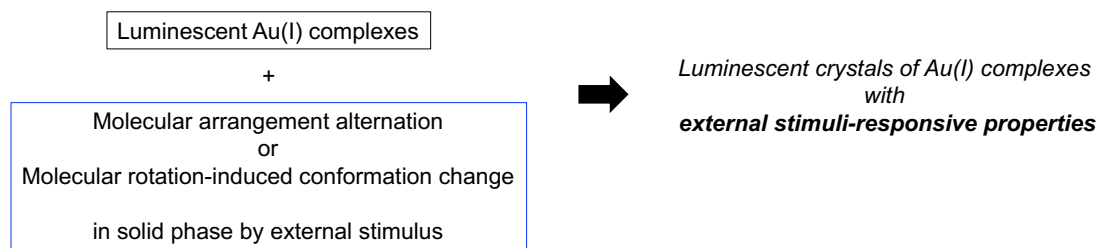


Figure 5. Representation of design concept for developing luminescent crystals of Au(I) complexes showing external stimuli-responsive properties.

2. External stimuli-responsive luminescence of Au(I) complexes via crystal structure change

2.1. Emission change from crystal to amorphous phase transition

In 2002, Fackler *et al.* reported a linear coordination polymer of Au(I) complex showing thermochromic and mechanochromic luminescence in a crystalline phase, which is the first example of the mechano-responsive luminescence of Au(I) complex (Figure 6a) [10]. The pristine crystals showed no emission, while a green emission appeared after mechanical grinding. Catalano *et al.* (2003) [11] and Esienberg *et al.* (2008) [12] also reported pioneering mechano-responsive luminescent crystals formed by binuclear Au(I) complexes, as shown in Figure 6a. These crystalline samples showed orange- or green emissions that aurophilic interactions could be involved in the process. Interestingly, blue-shifted emission was clearly observed when the crystals were mechanically ground. However, it is still unclear the mechanism of the mechanical stress-response emission alternation.

Ito *et al.* (2008) reported the first example of reversible mechanochromic crystal by using binuclear Au(I) isocyanide complex possessing penta-fluorobenzene moiety (Figure 6b and c) [13]. The initial crystal showed blue emission under UV light and clearly showed yellow emission when the crystal was gently ground. It is revealed that the crystalline phase was altered to amorphous by the mechanical grinding with the formation of aurophilic interactions, resulting in the red-shifted emission (Figure 6c). Interestingly, the amorphous ground phase could recover to the initial crystalline phase by adding CH₂Cl₂ solution to the solid sample. The same group reported that the advanced mechano- and solvent-responsive emission change by utilizing the analogous Au(I) complex **2** possessing tetra-fluoropyridine group instead of penta-fluorobenzene (Figure 6d and e) [14]. The initial crystalline phase **2B** showed blue emission and included acetone molecules in the crystal. Evaporation of **2B** under a low pressure produced green-emitting crystalline phase **2G**. Acetone molecules in the pristine crystals were released, resulting in slightly altered molecular arrangement with emission changes. Moreover, mechanical grinding to **2G** resulted in yellow emitting other crystalline phase **2Y** that no acetone inclusion was observed. Interestingly, further grinding procedure to **2Y** induced orange emitting amorphous phase **2O** (Figure 6e). Indeed, adding acetone to **2Y**

or **2O** gave the initial crystalline phase **2B**. The crystal structures of **2B**, **2G**, and **2Y** indicated that the red-shifted emission was caused by the formation of aurophilic interactions.

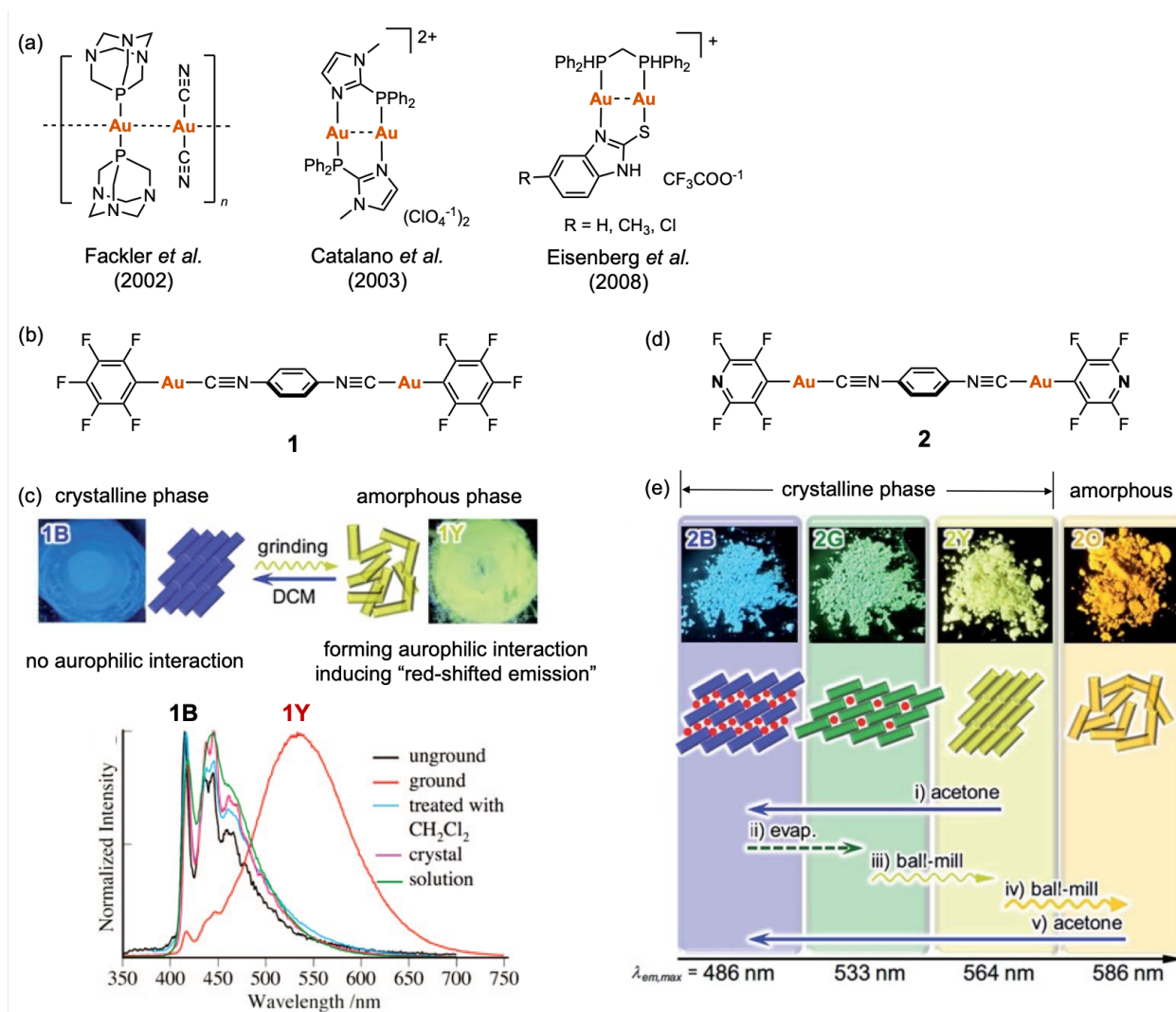


Figure 6. (a) Pioneering examples of Au(I) complexes showing mechano- or thermo-responsive luminescence in the solid phase. (b) Molecular structure of Au(I) isocyanide complex **1** and (c) the reversible mechanochromic properties. (d) Au(I) isocyanide complex **2** possessing tetra-fluoropyridine group and (e) the mechano- and solvatochromism based on the multiple-crystalline phases and amorphous phase.

Mechano-responsive properties of mono-nuclear Au(I) phenyl-isocyanide complexes has been intensely investigated by Seki and Ito *et al.* (Figure 7a). They reported a screening approach to investigate mechanochromism of Au(I) isocyanide complexes as well as solid-state phase transition via mechanical

stimulation [15]. Some electronically withdrawing or donating groups were substituted at the para-site of phenylene, and a total of 48 different Au(I) isocyanide complexes were investigated. Through observation of emission change and crystal structure transition, it was revealed that 26 mechanochromic Au(I) complexes were undergoing “crystal-to-amorphous” phase transition during the mechanical grinding. And, only two Au(I) isocyanide complexes exhibited “crystal-to-crystalline powder” phase transition with an apparent change in emission after mechanical grinding, which will be described in another section.

Most of the observed emission alternations occurred in the visible region. Nonetheless, the introduction of large π -conjugated moiety into Au(I) isocyanide complex induced largely red-shifted emission from the IR region via mechanical grinding (Figure 7b) [16]. Seki and Ito *et al.* reported that 9-anthryl Au(I) isocyanide complex **3** formed three different polymorphs, and one of them exhibited blue emission ($\lambda_{\text{em,max}} = 448 \text{ nm}$), showing mechanochromic properties that resulted in the IR emission ($\lambda_{\text{em,max}} = 900 \text{ nm}$) by just simple mechanical grinding. These were subjected to a “crystal-to-amorphous” transition, and the formation of aurophilic interactions with multi-intermolecular interactions in the resulted amorphous phase might induce the dramatically red-shifted emission change.

In general, rational design or prediction of molecular arrangements in molecular crystals is difficult. Even a slight difference in molecular structure can cause drastic structural changes in the crystal structures. Furthermore, there is no general idea for controlling the phase transitions of a crystal. To challenge this subject, Jin, Seki, and Ito addressed that utilizing axial chirality of molecule could provide a motif for modifying mechanochromic properties via distinct molecular packing modes between racemic and homochiral crystals (Figure 7c) [17]. Racemic and homochiral (here, *S*-) Au(I) isocyanide complexes with a binaphthyl moiety provided distinct crystal structures, resulting in different emissions. Interestingly, upon mechanical grinding, both two crystals changed to amorphous with orange emission, displaying distinct mechanochromic patterns. These results suggested that molecular chirality can be one of the tools for designing stimuli-responsive materials.

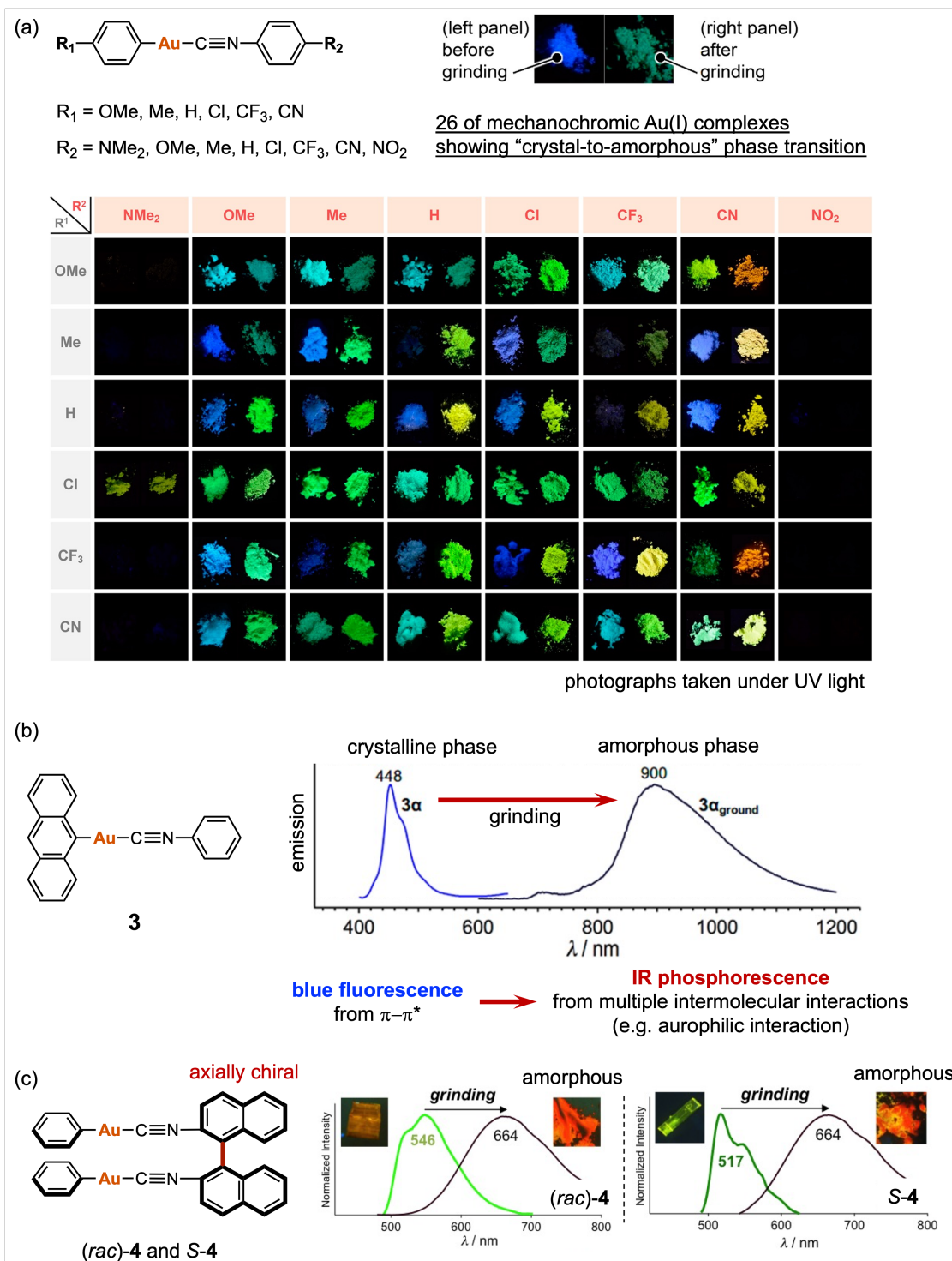


Figure 7. (a) Photographs of the 48 aryl Au(I) isocyanide complexes with mechanochromic properties under UV light. (b) 9-Anthryl Au(I) isocyanide complex **3** with the large red-shifted emission by mechanical grinding. (c) Racemic and *S*-Binaphthyl Au(I) isocyanide complex **4** with the distinct emission change properties via mechanical stress.

Many examples of mechanochromism of Au(I) complexes with “crystal-to-amorphous” phase transition upon mechanical grinding showed red-shifted emission change which is well defined as “bathochromic-shift.” Nevertheless, some Au(I) complexes could also show blue-shifted emission changes by grinding (called “hypochromic-shift”). As shown in Figure 8a, an Au(I) isocyanide complex **5** with a pendant carboxy group formed two polymorphs. One of the polymorphs showed blue emission with no aurophilic interaction, while the other polymorph exhibited red emission with strong aurophilic interactions in the crystal structure [18]. These crystals were converted to the same amorphous phase showing green emission, which suggested that relatively moderate aurophilic interactions were present in the ground phase.

Utilizing *N*-heterocyclic carbene ligand into Au(I) complexes produced luminescent mechanochromism behavior with hypso- and bathochromic spectral shifts (Figure 8b). Two analogous NHC Au(I) complexes **6** and **7** possessing 1,3-diisopropylbenzimidazole or naphthimidazole moiety on the NHC ligands were synthesized. These compounds showed distinct molecular packing manners in the crystals [19]. The both two crystals exhibited “crystal-to-amorphous” phase transition through mechanical grinding with both blue-shifted or red-shifted emission changes.

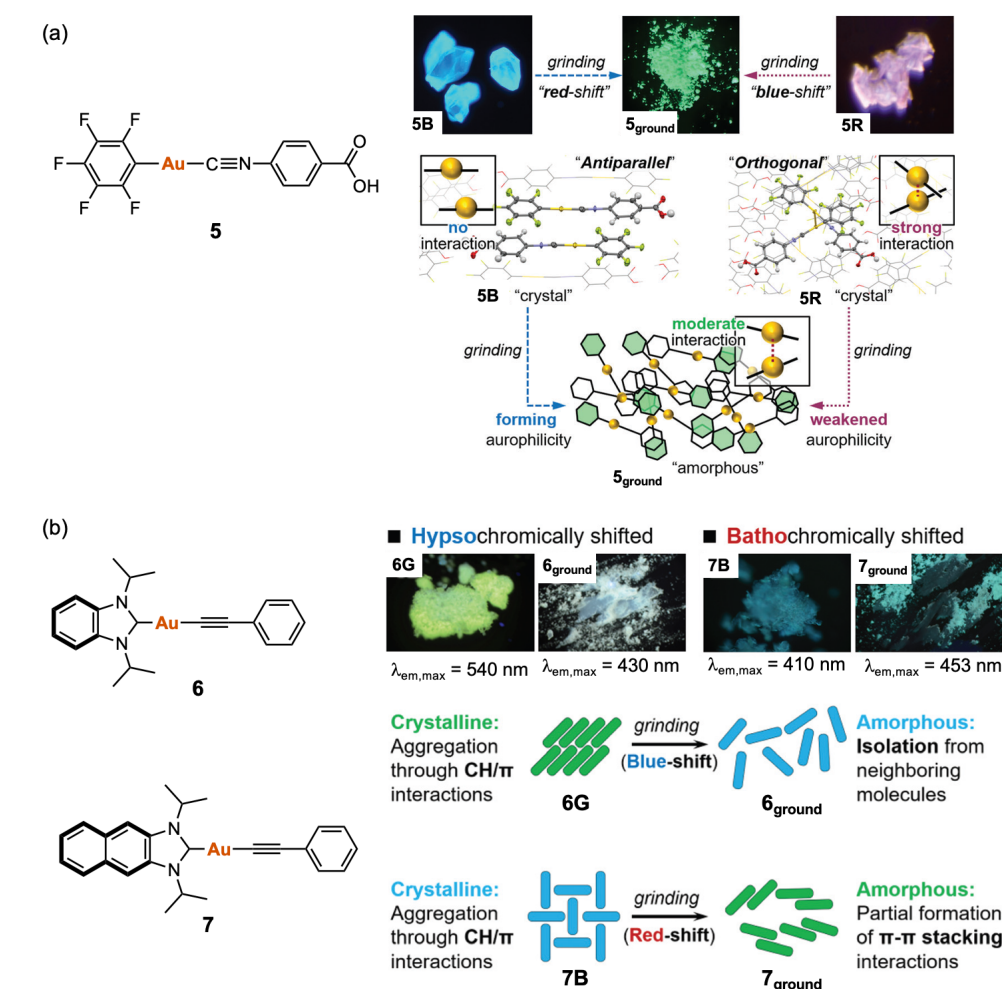


Figure 8. (a) Au(I) isocyanide complex **5** possessing carboxyl moiety with the blue- and red-shifted mechanochromic polymorphs. (b) NHC Au(I) complexes **6** and **7** showing hypso- and batho-chromical shift by mechanical grinding.

Based on our aforementioned studies on aryl Au(I) isocyanide complexes, it could be envisioned that the Au(I) isocyanide complexes were a promising candidate for solid-state emitting materials that can response to volatile molecules. Through the intense studies by the Ito group, it has been revealed that aryl Au(I) isocyanide complexes tend to form multiple crystalline structures with distinct emission colors and show solid-state phase transition via mechanical or thermal stimulations. Next, further molecular design for the formation of various crystalline phases was carried out to broaden the variety of stimuli-responsive solid-state emission. Seki and Ito *et al.* reported the development of a dinuclear Au(I) complex **8** in which the two aryl Au(I) moieties were bridged by biphenyl bis-isocyanide ligand, adopting various molecular conformations in solid-state [20]. This Au(I) complex could form eleven distinct crystal structures by including solvents or small organic molecules with different emission maxima ranging from blue to yellow emission colors (Figure 9a–d). The solvate crystals were converted to an amorphous phase showing yellow emission upon mechanical grinding (Figure 9b). The ground sample contained no solvent molecules and worked as pre-prepared states to respond with solvent inclusion. The addition of various solvents or small organic molecules followed by drying under ambient conditions yielded 11 different crystal structures, where the solvent corresponded to added solvents as follow: CHCl₃, pyridine (Py), CH₂Cl₂, CH₂Br₂, dimethylacetamide (DMA), acetaldehyde (AcH), CH₃CN, DMF, (*S*)-propylene oxide (*S*-PO), *rac*-propylene oxide (*rac*-PO), or acetone (Figure 9b and d).

In addition, Seki and Ito *et al.* reported the first example of porous molecular crystals that were assembled through aurophilic interactions of bent aryl Au(I) isocyanide complex **9**. This molecule showed molecular incorporation ability in the crystal with response to 26 different guest molecules (Figure 9e–g) [21]. These host-guest complexes in the crystalline phase showed chromic luminescence with both blue- and red-shifted emissions. Moreover, this porous organometallic crystal could exhibit luminescent mechanochromism by releasing the guest molecules (Figure 9h).

In Figure 10, the recent examples of stimuli-responsive Au(I) complexes are summarized. Numerous examples of mechano-responsive luminescent crystals of Au(I) complexes exhibited emission alternation based on “crystal-to-amorphous” phase transitions (Figure 10) [22–39]. This suggested that macro-scale mechanical grinding could affect the micro-scale order of the molecular packing structure of Au(I) complexes in the solid-state. The mechanical stress tended to increase the entropy of the molecular arrangement that results in the formation of the amorphous phase after the grinding process.

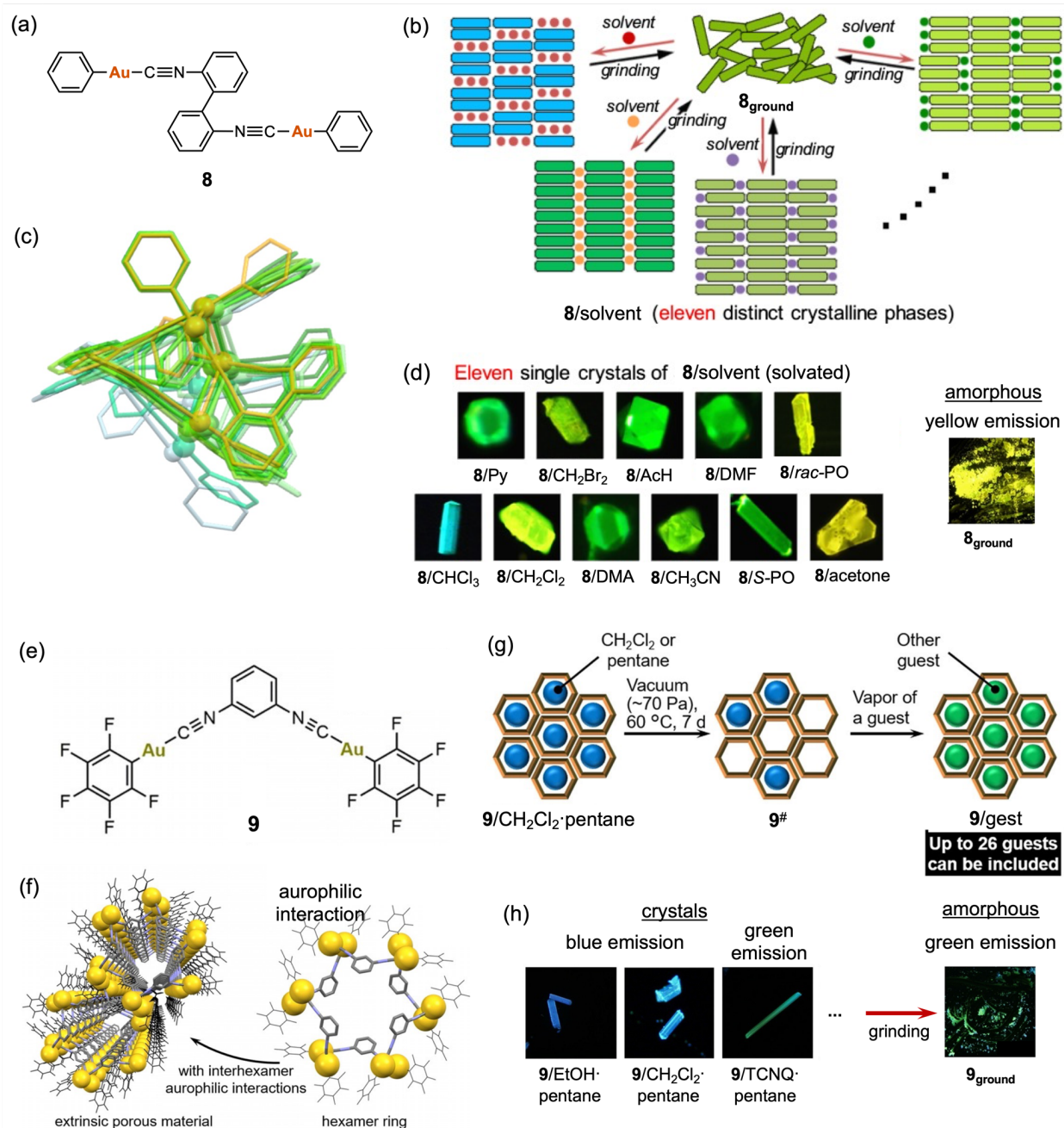
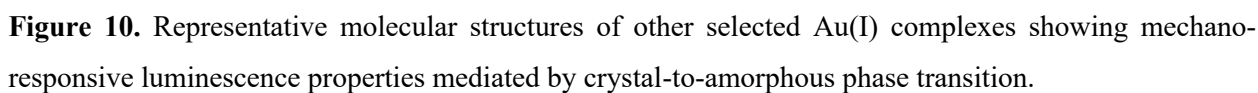


Figure 9. (a) Au(I) biphenyl isocyanide complex **8** and (b) the variety of solvato- and mechanochromic properties. (c) Overlapped dimer structures of **8** in (d) the eleven solvate single crystals. (e) Bent structure of Au(I) isocyanide complex **9** forming (f) porous crystalline structure via aurophilic interactions. (g) Applying up to 26 guest molecules in the crystal and (h) the observed emission change via mechanical stress.



2.2. Emission change resulting from crystal-to-crystalline powder (C-to-C powder) phase transitions

A crystal-to-crystalline powder (C-to-C powder) phase transition has been reported as a distinct regime of solid-state luminescence alternating with external stimulations. The transition can provide a molecular-level understanding of the correlation between the solid-state emission and the structural information given by powder and single-crystal XRD with phase transition. In the case of mechano-responsive crystals, the initial crystalline samples (single crystals or crystalline particles) were cracked to powder samples due to the mechanical grinding. And examples of “crystal-to-amorphous” phase transition were far more than those of “crystal-to-crystalline powder” phase transition [1]. From the screening approach of aryl Au(I) isocyanide complexes with modifying *para*-substitution by Ito group (Figure 7a), only two examples exhibited mechanochromic properties via “crystal-to-crystalline powder” phase transition while 26 examples of mechanochromic Au(I) complexes were undergoing “crystal-to-amorphous” transitions [15]. Blue emitting crystal prepared from phenyl Au(I) isocyanide complex **10** showed an alternation of emission to yellow emission through mechanical stress or thermal heating (Figure 11a). Powder and single-crystal XRD analysis of the starting and resulting samples revealed that the yellow emitting solid retained crystallinity. Interestingly, significant intermolecular aurophilic interactions were observed in the resulted phase, which would cause the red-shifted emission. Analogous Au(I) complex **11** formed a green-emitting crystal that shows mechanochromism with apparent red-shift emission to orange color (Figure 11b) [15]. The ground sample was in a crystalline phase, and a clear formation of aurophilic interactions in the crystal was observed. These results strongly suggested that the aurophilicity in the crystalline phase plays an important role in the red-shift emission change after external stimulations.

The design of a meta-stable phase is a key concept for stimulation-responsive materials because the meta-stable phase can transform to a more thermodynamically stable phase upon external stimulation. Nevertheless, there exists an issue on the rational design of a metastable crystalline phase and controlling the phase transition accompanied by the emission alternation. Regarding chirality of crystal, it is known that homo-chiral crystal typically formed a thermodynamically less stable crystalline phase rather than the corresponding racemic crystal, which has been known as “Wallach’s rule.” Jin, Seki, and Ito demonstrated the biphenyl isocyanide Au(I) complex **12** to design a “crystal-to-crystal” phase transition with an emission change response to mechanical stress by exploring the aforementioned thermodynamic stability difference in the chirality of crystal (Figure 11c) [40]. The green-emitting crystals were constructed by columnar structure including infinitely interacted aurophilicity and formed chiral crystal possessing the chiral space group $P2_12_12_1$. Through mechanical grinding of the chiral crystal, it was observed that clear emission decreases, and the “crystal-to-crystalline powder” phase transition to an achiral crystal possessing $P-1$ space group (Figure 11c).

There have been many reported examples of mechanochromism at ambient temperature. Seki and Ito *et al.* reported a luminescent mechanochromism only observed in low-temperature of thienyl Au(I) isocyanide complex **13** based on “crystal-to-crystal” phase transition (Figure 11d) [41]. The as-prepared crystalline powder of this complex did not show any luminescent color changes upon grinding at room temperature. When it was cooled below $-50\text{ }^{\circ}\text{C}$, the sample showed a blue emission. Upon grinding this powder at below $-50\text{ }^{\circ}\text{C}$, a green emission was observed to form a new crystalline phase.

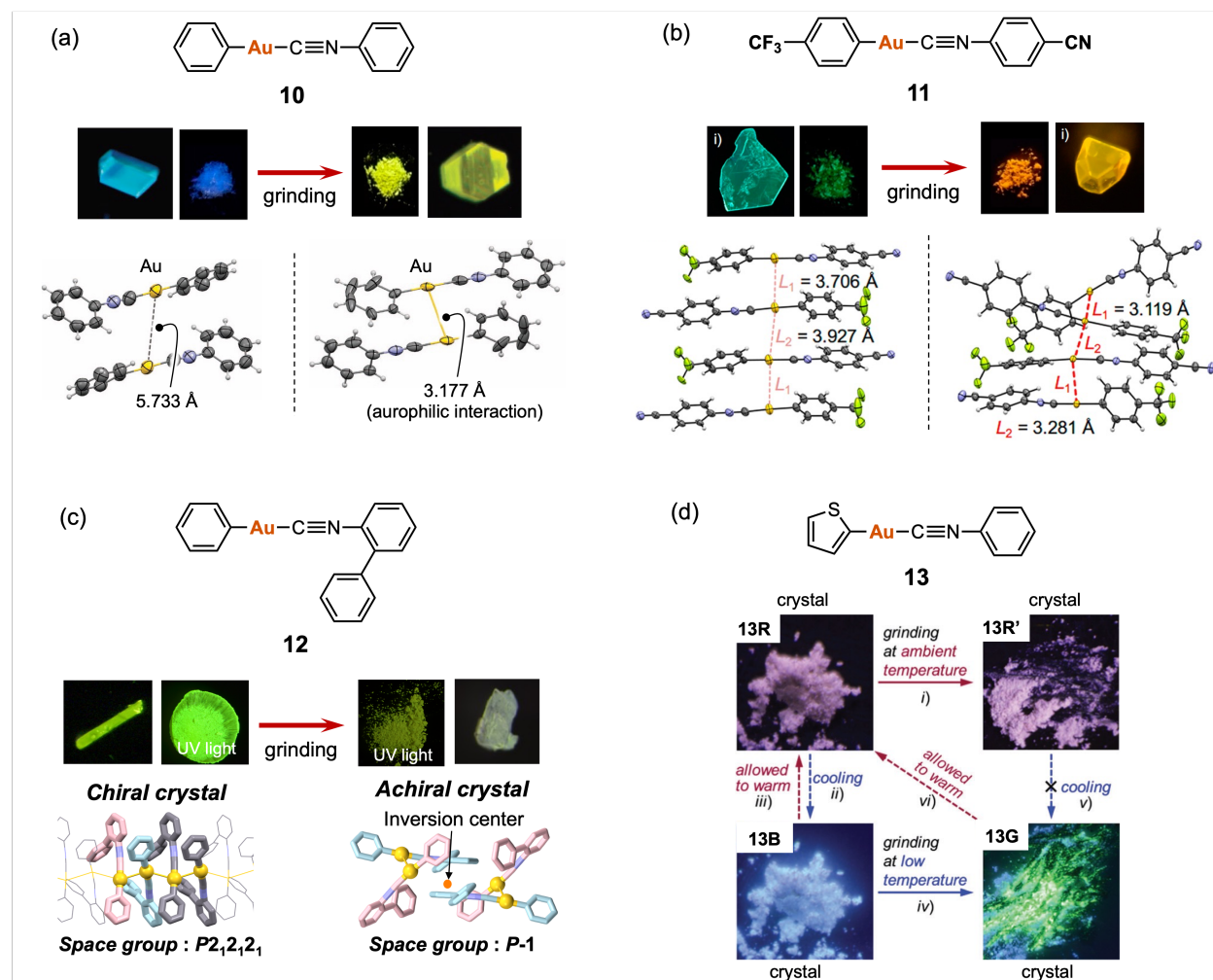


Figure 11. (a) Phenyl Au(I) isocyanide complex **10** and (b) its derivative **11** showing the mechanochromic properties via crystal-to-crystal phase transition. (c) Au(I) biphenyl isocyanide complex **12** showing chiral-crystal-to-achiral-crystal phase transition via mechanical grinding. (d) Thienyl Au(I) isocyanide complex **13** with mechanochromism at a low temperature.

Yagai and Ito *et al.* succeeded in constructing meta-stable crystalline phase of Au(I) isocyanide complexes by introducing triethylene glycol (TEG) derivate chains in the Au(I) complex (Figure 12a)

[42,43]. The authors expected that the segregated aggregation of the rigid luminophore unit and flexible TEG units of the Au(I) complex would facilitate mutual phase transitions between crystalline and amorphous phases upon thermal treatment. Interestingly, the introduction of TEG chains induced a “transient” amorphous phase that continuously undergoes a phase transition towards another crystalline phase. The initial crystalline phase **14B** showed a red-shifted emission change to yellow color (**14Y**) by mechanical grinding. After several seconds from the alternation, the ground **14Y** phase changed to the green-emitting new crystalline **14G** phase at room temperature. (Figure 12b). Single-crystal XRD studies of the blue and green-emitting crystals revealed that the layered structures between rigid Au(I) isocyanide complexes and TEG aggregated region can operate to re-construct of crystal structure from the amorphous phase due to mechanical grinding as well as the red-shifted emission caused by the formation of aurophilic interactions (Figure 12c–d). In addition, fine-tuning of the lifetime of the transient phases of mechanochromic Au(I) complexes were achieved by modifying the terminal groups of their TEG side chains (Figure 12b) [43].

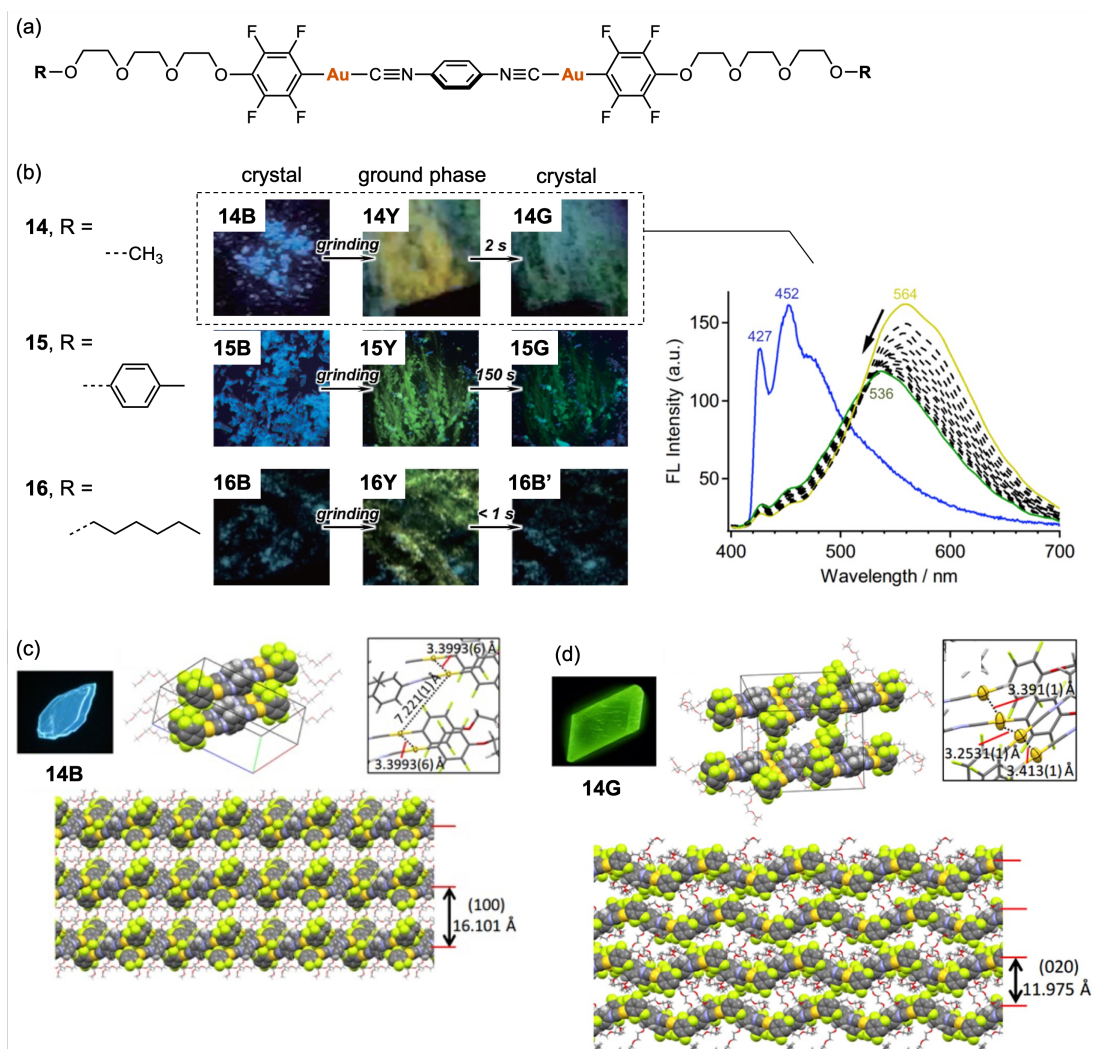


Figure 12. (a) Au(I) isocyanide **14**, **15**, and **16** possessing TEG side chains. (b) Observed variety of transient mechanochromic changes from blue to green emission. Crystal structures of (c) the blue and (d) green-emitting crystals.

Laguna and Fackler *et al.* reported a pioneering vapochromic Au(I) complex **17** that the Au atoms were bonded with Tl(I) atoms in the crystalline phase (Figure 13a) [44]. The crystalline powder displayed emission changes when the solid was exposed to various organic vapors such as acetone, acetonitrile, triethylamine, THF, pyridine, etc. The resulted samples showed emission color change back to that of starting phase upon heating to 100 °C. During the exposure to vapors and heating of the samples, the major crystalline phases were persisted, while the partial domain near the Au(I) and Tl(I) atoms might be slightly changed, inducing some change of the intermetallic interactions that can influence the luminescence properties.

Yam *et al.* developed decanuclear Au(I) sulfido complexes **18** displaying multi-stimuli-responsive luminescence changes based on “crystal-to-crystal” phase transitions between distinct pseudo-polymorphs (Figure 13b) [45]. The as-prepared crystal, which showed blue emission exhibited mechanochromism altered to green-emitting crystalline phase **18G**. Several organic solvents induced the clear emission changes of **18G**. Especially, adding MeOH produced clearly different polymorphs exhibiting red-colored emission. All the crystal samples formed by solvent addition were reversely changed to **18G** by mechanical grinding.

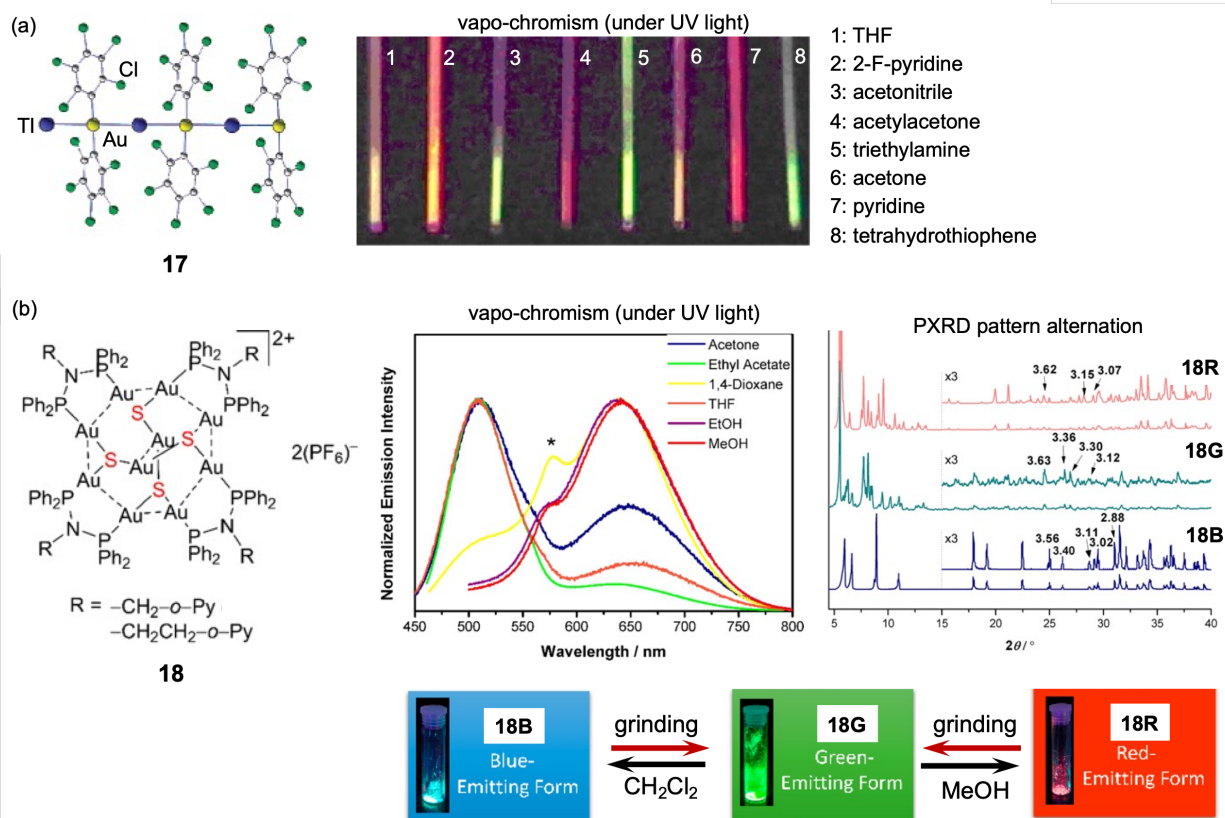


Figure 13. (a) Vapochromic Au(I) complex **17** response to 8 different solvents. (b) Decanuclear Au(I) sulfido complexes **18** displaying multi-stimuli-responsive luminescence changes.

2.3. Emission change resulting from single-crystal-to-single-crystal (SCSC) phase transitions

In 2013, Ito *et al.* reported the first example of a mechano-triggered single-crystal-to-single-crystal (SCSC) phase transition with a change in its photoluminescence using phenyl Au(I) isocyanide complex **10** (Figure 14a–b) [46]. The blue emitting single crystal (**I_b**) formed no aurophilic interactions, and a change in emission to yellow color was observed where small mechanical pricking was applied. Interestingly, the yellow emitting domain was propagated from the pricking part to the whole of the crystal. Single-crystal XRD revealed that the resulted yellow emitting crystal (**II_y**) formed a totally different crystal structure compared to the initial blue-emitting crystal. Particularly clear intermolecular aurophilic interactions were observed in the yellow emitting crystal, which indicates that the red-shifted emission was due to the formation of aurophilic interaction (Figure 14b). The author also found that the same SCSC transformation was achieved by contacting a seed crystal **II_y** to other crystals in **I_b** polymorph (Figure 14b). In addition, heating the initial crystal (**I_b**) changed to the yellow emitting crystals (**II_y**), indicating that the **II_y** was a thermodynamically stable phase rather than the crystal **I_b**. Similarly, the Ito group developed the mechano-induced SCSC phase transition with emission change using the dimethyl-substituted analog of Au(I)

isocyanide complex **19** (Figure 14a and c) [47]. In this case, the green-emitting single crystal (**I_g**) having strong aurophilic interactions converted to the blue-emitting single crystal (**II_b**) that had no aurophilic interaction by mechanical stress as well as simple contact of a resulted crystal to an initial polymorph crystal (Figure 14c).

The mechano-induced SCSC transition of **10** and **19** showed no direct reversibility from the resulted phase to the initial structure in an SCSC manner. However, Jin, Seki, and Ito *et al.* reported the first example of a mechano-induced SCSC transition of Au(I) isocyanide complex **19** accompanied by emission color change (Figure 14d-f) [48]. The Au(I) complex formed MeOH included single crystals and exhibited SCSC phase transition upon mechanical pricking with drastic emission color change from green to orange under simultaneous release of MeOH from the crystal lattice (Figure 14e). In the previous mechano-induced SCSC phase transition of **10** and **19**, the key factors were the phase transition from metastable to stable phases. In this work, the key feature for the reversibility was the release/inclusion of MeOH in the crystal. Indeed, it was reasonable to assume that the initial crystal structure forms a polar space group with having a polar solvent (MeOH) network channel. After releasing the MeOH molecules, its crystal structure changed to a nonpolar phase, where the molecular polarity was canceled by the centrosymmetric structure with an inversion center (Figure 14f).

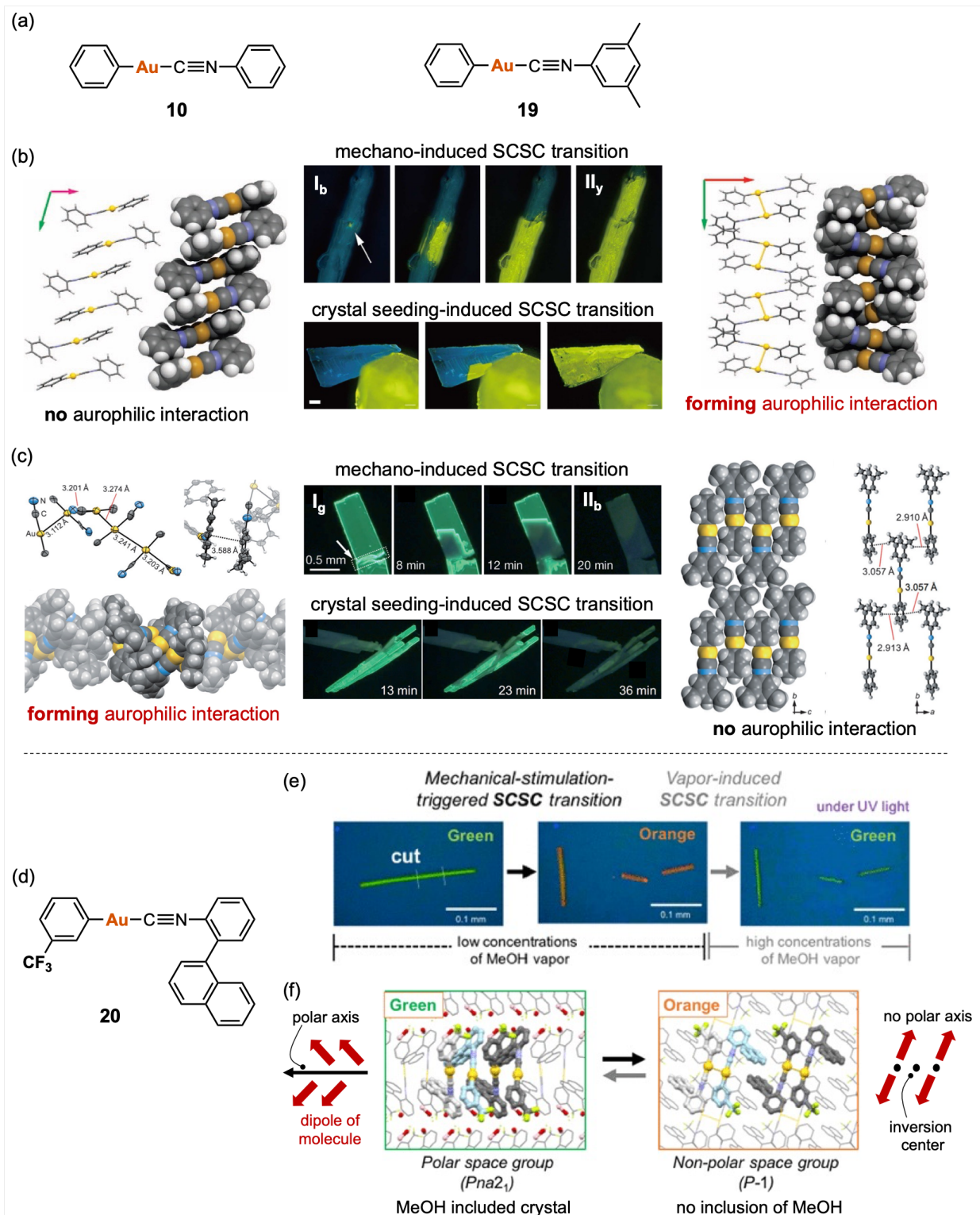


Figure 14. Mechano-triggered and crystal-seeding-induced SCSC phase transition with emission alterations of (a) Au(I) isocyanide complexes (b) **10** and (c) **19**. (d–f) Reversible SCSC transition with emission change by mechanical pricking and MeOH vapors of Au(I) complex **20**.

Ito *et al.* reported the first example of photo-induced SCSC phase transition of Au(I) complex that involved the enhancement of intermolecular aurophilic interactions with emission color change (Figure 15) [49]. Blue-emitting single crystals were constructed from synthesized Au(I) isocyanide complex **21** constructed, including weak intermolecular aurophilic interactions (distance of Au–Au=3.5041(4) Å, Figure 15b and e). UV light (365 nm) irradiation to the blue-emitting crystal-induced a clear red-shifted emission change to yellow color based on a photo-induced SCSC phase transition (Figure 15b). The resulting yellow-emitting crystal formed strong aurophilic interactions (distance of Au–Au=3.2955(6) Å, Figure 15f). Interestingly, the UV irradiation to the initial crystals also induced crystal jumping or cracking, so-called as “photo-salient effect” (Figure 15c). In addition, the initial blue-emitting crystal could convert to the yellow-emitting crystalline phase by mechanical grinding (Figure 15d) [50].

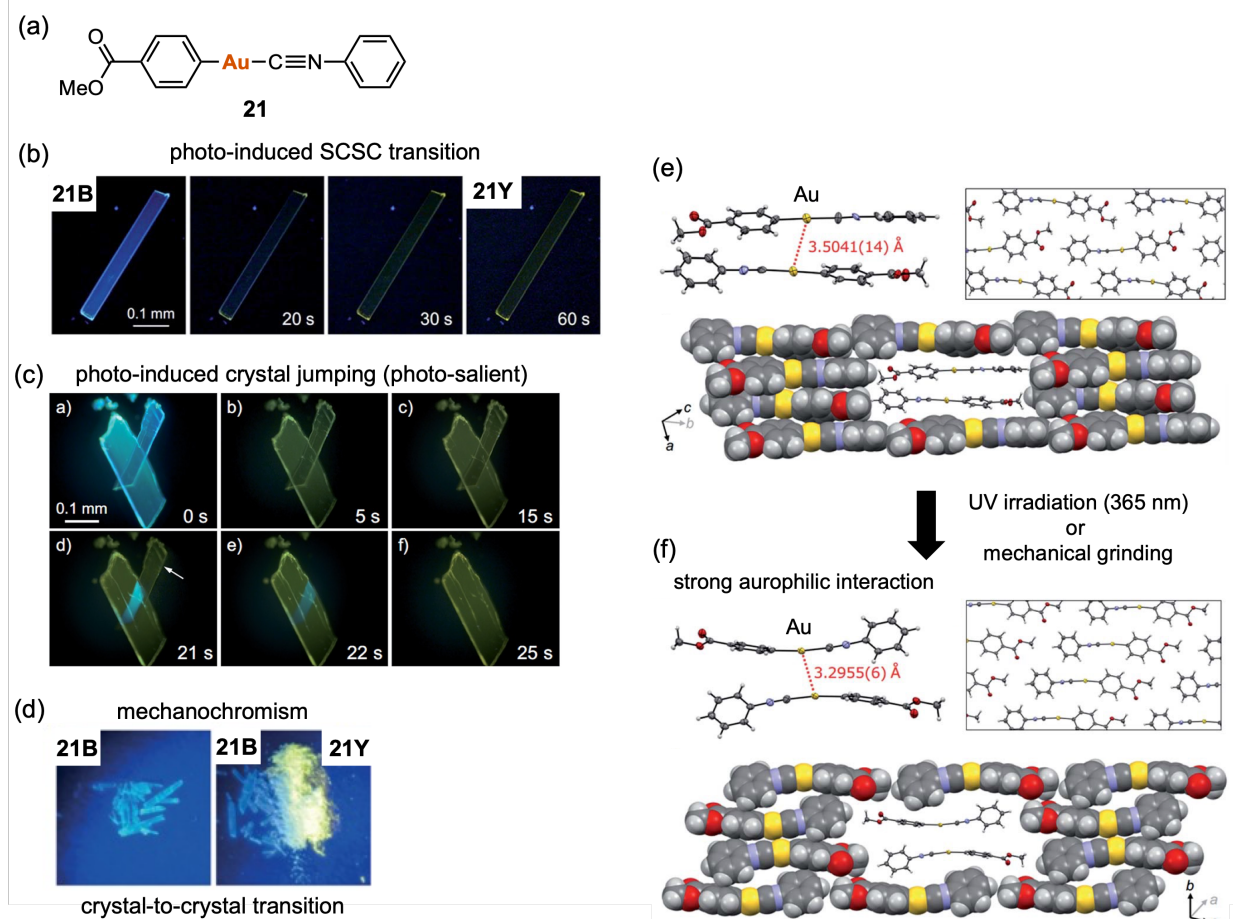


Figure 15. (a) Molecular structure of Au(I) isocyanide complex **21**. (b) Observed photo-induced SCSC phase transition with emission change and (c) photo-salient effect. (d) Mechanochromic properties of the initial crystals. Confirmed crystal structures of (e) the initial and (f) resulting single crystals.

The pioneering example of a reversible thermal-induced SCSC phase transition of Au(I) complex accompanied by an emission color change that correlated with association/dissociation of aurophilic interactions was reported by Balch *et al.* in 2005 (Figure 16a–b) [51]. The trinuclear Au(I) cluster organometallic complex **22** formed red-colored emitting crystals having an emission-maxima at 667 nm under room temperature. On cooling the crystal, the emission spectrum was significantly altered, as described in Figure 16b. At a low temperature (77 K), two emission maxima at 490 nm and 680 nm were observed. The packing mode of two trimeric Au(I) complexes at room temperature was slightly altered to form two distinct structure types of the Au(I) clusters, one of which was forming aurophilic interaction and the other was dissociating Au–Au distance. Changes in these structural environments could be correlated with alternations in the emission spectra.

Omary *et al.* reported macrocyclic trinuclear Au(I) complex **23** that formed NIR emitting crystal (emission maxima at 700 nm) at room temperature [52]. In the crystal, two Au(I) complexes stacked together with forming intermolecular aurophilic interactions. Upon cooling the crystal below 140 K, the crystal showed a blue-shifted emission (emission maxima at ca. 495 nm) with SCSC transition based on the unit cell shrinking (Figure 16c).

Balch *et al.* reported thermochromic properties of the luminescent single crystals formed by Au(I) cationic complex **24** $[\text{C}_6\text{H}_{11}\text{NC})_2\text{Au}]^+$ with combinations of several counter anions (Figure 16d) [53]. Octahedral anions (PF_6^- , AsF_6^- , SbF_6^-) could be used to construct distinct packing structures of the Au(I) complexes with a different mode of intermolecular aurophilic interactions in the crystals. Blue-emitting crystals of $[\text{C}_6\text{H}_{11}\text{NC})_2\text{Au}](\text{PF}_6)_{0.50}(\text{AsF}_6)_{0.50}$ were formed by the Au(I) complex **24** containing PF_6^- and AsF_6^- anions and showed luminescence change from blue to green by heating to 377–381 K in SCSC transition manner (Figure 16d).

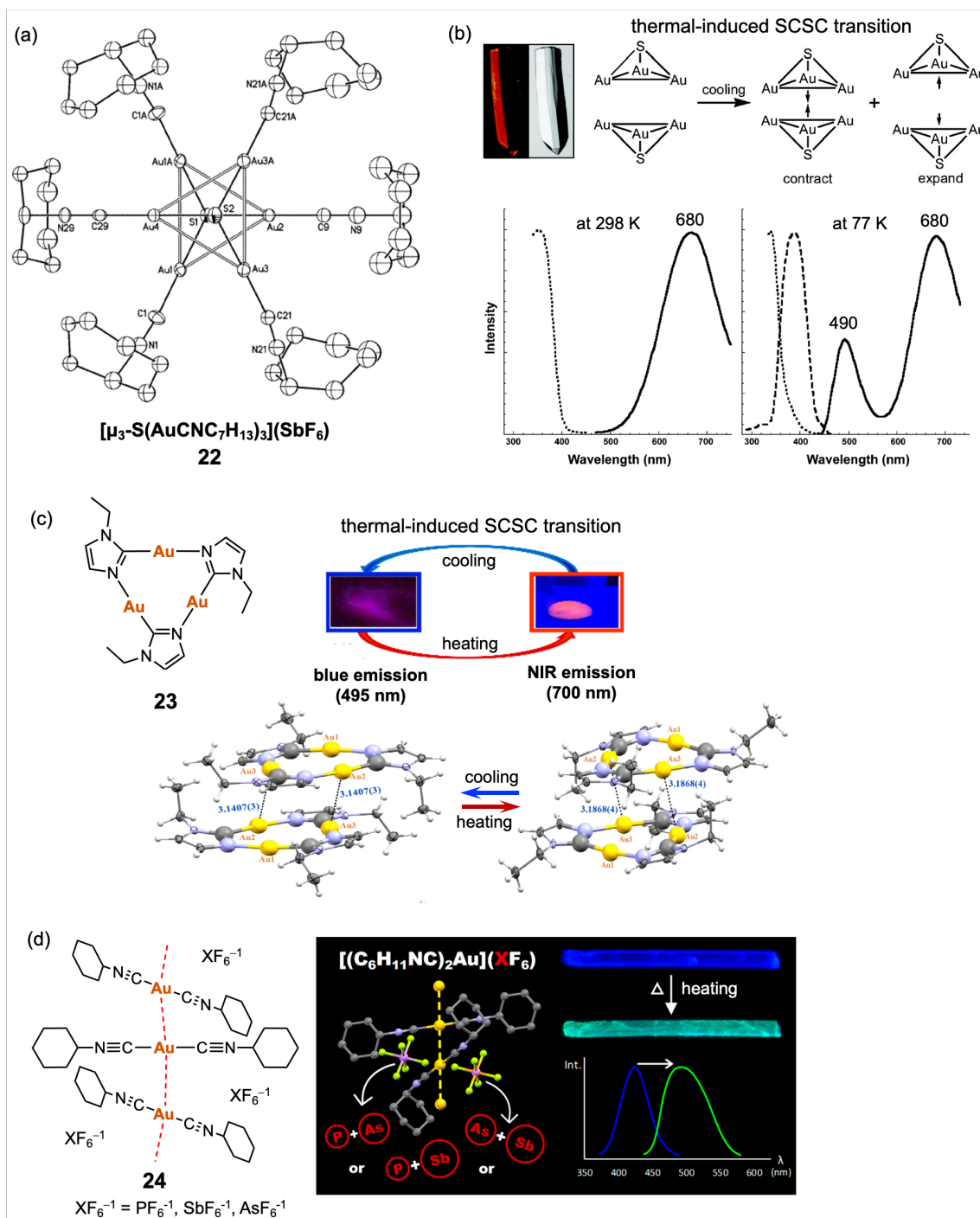


Figure 16. (a) The trinuclear Au(I) cluster organometallic complex **22** and (b) the thermal-induced SCSC transition with emission spectra change. (c) An macrocyclic trinuclear Au(I) complex **23** showing NIR at room temperature and drastic blue-shifted emission via cooling the single crystals. (d) Thermochromic single crystal of Au(I) cation complex $[(\text{C}_6\text{H}_{11}\text{NC})_2\text{Au}]^+$ (**24**) with combinations of counter anions species.

3. External stimuli-responsive luminescence of Au(I) complexes via molecular rotation in crystal

The luminescent properties of molecular crystals strongly correlate with the luminophore arrangement and the structural conformations in solid-state. In other words, utilizing molecular rotation in solid-state could be one of the motifs to design stimuli-responsive solid-state luminescence. Recently, Jin, Ito and Garcia-Garibay *et al.* reported the first example of solid-state phosphorescence controlled by molecular rotation in crystalline phase using a dumbbell-shaped Au(I) complex **25** (Figure 17a–c) [54]. The central phenylene worked as the rotator, and the bulky phosphine ligand was introduced as the stator. The formed luminescent amphidynamic crystal showed ca. 4.00 MHz rotational frequency for the rotator rotation with green emission at room temperature (Figure 17b). Upon cooling the crystal, the rotational motion turned to static as well as the emission color changed to yellow. Emission spectra under variable temperature indicated that the broad emission component near 543 nm was phosphorescence and clearly showed emission enhancement by lowering the temperature. The crystal structure of **25** revealed that the Au(I) complexes infinitely constructed zig-zag intermolecular packing with aurophilic interactions (Figure 17c). The authors addressed that intermolecular electronic conjugation was formed through the aurophilic interaction and cleaved by rotational motion of the central phenyl-ring of the Au(I) complex in the crystal. As described in Figure 17c, the phosphorescence emission and the rotator rotation in the crystal occurred in the same time scales (e.g., 10^{-6} to 10^{-3} s), such that changes in rotational motion could modulate orbital interactions between adjacent chromophores, altering the excitation process.

As a next step in efforts to prepare stimuli-responsive crystalline materials, the authors prepared and analyzed the properties of the analogous isomorphous structure of Au(I) complexes **26** and **27**, which featured a polar 2,3-difluorophenylene or tetra-fluorophenylene rotator, respectively (Figure 17d) [55]. The Au(I) complexes also formed crystal structures having the zig-zag intermolecular packing manner with aurophilic interactions. The crystals showed similar emission alternation via temperature change as well as molecular rotation frequency change. Interestingly, these crystals did not undergo a phase transition upon changing the temperature. However, they showed significant anisotropy in their thermal expansion coefficients, corresponding to the molecular rotation in the crystal (Figure 17e). Furthermore, the luminescent amphidynamic crystals showed “salient effects” upon drastic temperature change, indicating that such examples have generated opportunities to transduce molecular-level rotation events into macroscopic phenomena, such as the jump of crystals (Figure 17f).

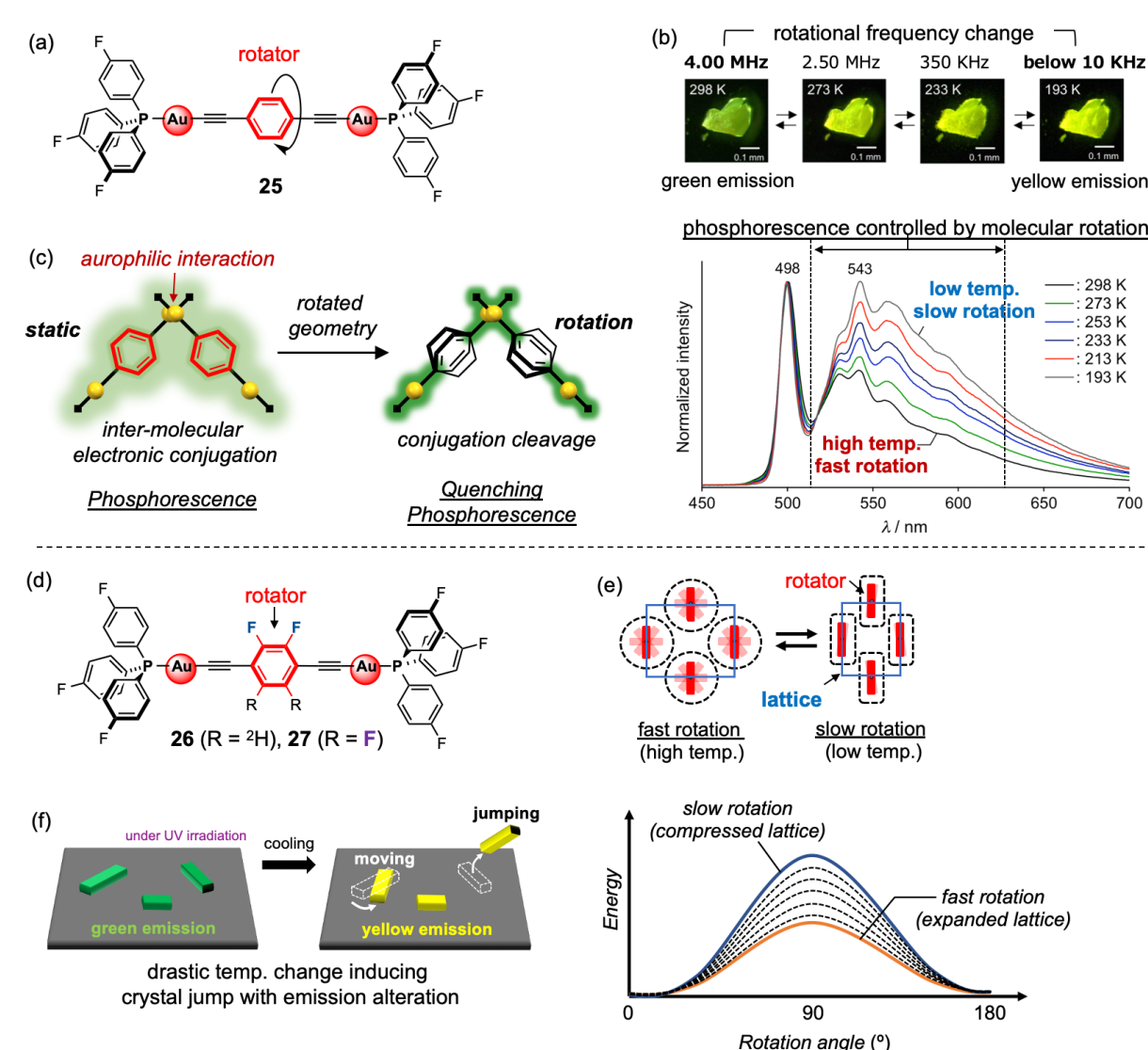


Figure 17. (a) Designed dumbbell-shaped Au(I) complex **25** and (b) the luminescent amphidynamic crystals showing thermochromic properties accompanying the rotational frequency change. (c) Representation of the correlation between molecular rotation and phosphorescence. (d) Analogous dumbbell-shaped Au(I) complexes **26** and **27** possessing fluorine atoms on the central phenylene rotator. (e) Schematic representation of the correlation between molecular rotation and the anisotropic expansion of crystal lattice. (f) Thermochromic emission change and salient effects via cooling the crystals.

Very recently, Jin and Ito *et al.* developed a novel platform for designing emissive crystalline molecular rotors using concave-shaped NHC metal complexes possessing Au(I) or Cu(I) atoms as the metal moiety (Figure 18a–b) [56]. In the case of Au(I) complex **28**, the central pyrazine rotator showed ca. 5.00 MHz rotation at room temperature with 7.6 kcal/mol of rotational barrier in the crystalline media. The crystal exhibited blue emission under UV light irradiation at room temperature. At low temperature, the

emission enhancement was observed (Figure 18c). The emission lifetime was ca. 0.87 μ s, indicating the involvement of excited triplet states in the emission process. In addition, the authors noted that the rotational dynamics of the pyrazine rotator turned in slower during this cooling, and the phosphorescence occurred near the range of the time scale for the rotations (ca. 0.3 μ s for the Au(I) rotor at room temperature). From TD-DFT calculation using the crystal structure of **28**, the contributed molecular orbitals to excitation process were identified as transitions from HOMO and HOMO-6 to LUMO (Figure 18d). The obtained molecular orbitals indicated that photoexcitation of the Au(I) rotor **28** in the crystal was characterized as a ligand-to-ligand with entanglement of metal charge, which could be profoundly influenced by the geometry of the central pyrazine rotator (Figure 18d).

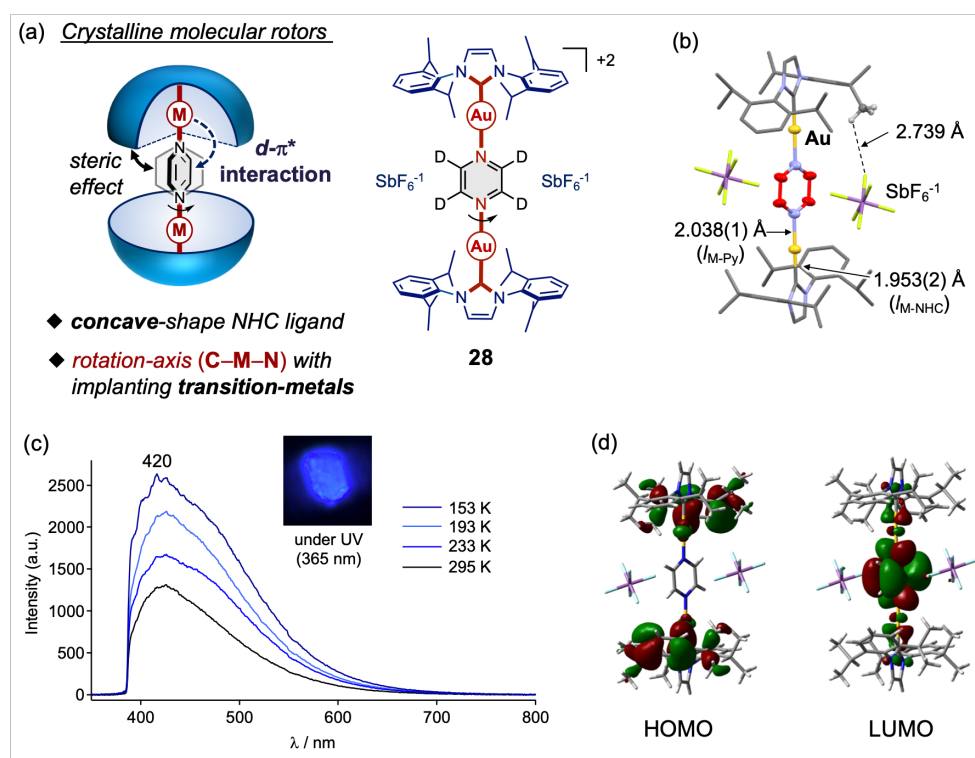


Figure 18. (a) Design concept and molecular structure of NHC Au(I) rotor **28**. (b) Confirmed crystal structure of **28** and (c) the observed solid-state emission with cooling-induced emission enhancement. (d) Frontier molecular orbitals obtained by TD-DFT calculation of the Au(I) rotor **28** in crystals.

4. Conclusion and future perspectives

This review described several examples of Au(I) complexes exhibiting solid-state luminescence with external stimuli-responsive properties (mechanical grinding, solvent addition, temperature change, and photo-irradiation), which were categorized in series of crystal phase transitions and molecular rotation in solid media. We could note that many examples of mechano-responsive solid-state luminescence were driven by “crystal-to-amorphous” phase transition. Even few examples of “crystal-to-crystal” or “single-crystal-to-single-crystal” phase transition induced by external stimulus, the molecular-level crystal structure information indicated that formation/deformation of auophilic interactions is crucially involved in determining the changes in emission properties. In addition, the molecular geometries near the Au(I) atom also worked as a key factor to control the solid-state luminescence, which can be altered by molecular rotation. Comparing to other luminescent metal complexes, Au(I) complexes afforded many examples of the stimuli-responsive solid-state emission alteration upon complexation with the organic ligand scaffolds. These might be origin from two significant features. One is a relatively good chemical stability of the Au(I) complexes, which gives a chance to handle the samples in an ambient environment. The other is the linear geometry of Au(I) complexes, which afford a high chance to form intermolecular auophilic interactions that highly affect the solid-state emission properties. In comparison to the examples showing the molecular arrangement changes by solid-state phase transition, utilizing molecular rotation in crystals are still rare, and the studies in the luminescent crystalline molecular rotors are at a preliminary stage; thus, further in-depth studies are required to deepen the design strategy with the dynamic behavior of the molecules for the responsive Au(I) crystalline materials.

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6. Biographical information of the authors

Prof. Dr. Mingoo Jin

Mingoo Jin was born in 1989 in Suwon (South Korea). He studied mechano-responsive luminescent crystalline materials using Au(I) isocyanide complexes under the guidance of Prof. Hajime Ito at Hokkaido University and received his Ph.D. in 2018. He moved to the University of California Los Angeles, where he has served Postdoctoral research regarding the development of luminescent crystalline Au(I) rotors under the supervision from Prof. Miguel A. Garcia-Garibay. Then, he started an academic career as an assistant professor at Hokkaido University in 2019. His current research interest is the design of novel crystalline molecular rotors via organometallic compounds with functional properties in solid-state.

Prof. Dr. Hajime Ito

Hajime Ito was born in 1968 in Osaka (Japan). He received his Ph.D. in 1996 under the guidance of Prof. Yoshihiko Ito at Kyoto University. He then joined the research group of Prof. Akira Hosomi at Tsukuba University before moving to Institute for Molecular Science in Okazaki in 1999. After he moved to The Scripps Research Institute as a visiting researcher of the research group of Prof. Kim D. Janda, he joined the research group of Prof. Masaya Sawamura at Hokkaido University in 2002. In 2010, he was appointed full professor. His research interests are the development of new organic synthesis methods and materials.

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