Angewandte Communications

VIP Molecular Domino Mechanism

DOI: 10.1002/anie.201307672

Controlling Mechano- and Seeding-Triggered Single-Crystal-to-Single-Crystal Phase Transition: Molecular Domino with a Disconnection of Aurophilic Bonds**

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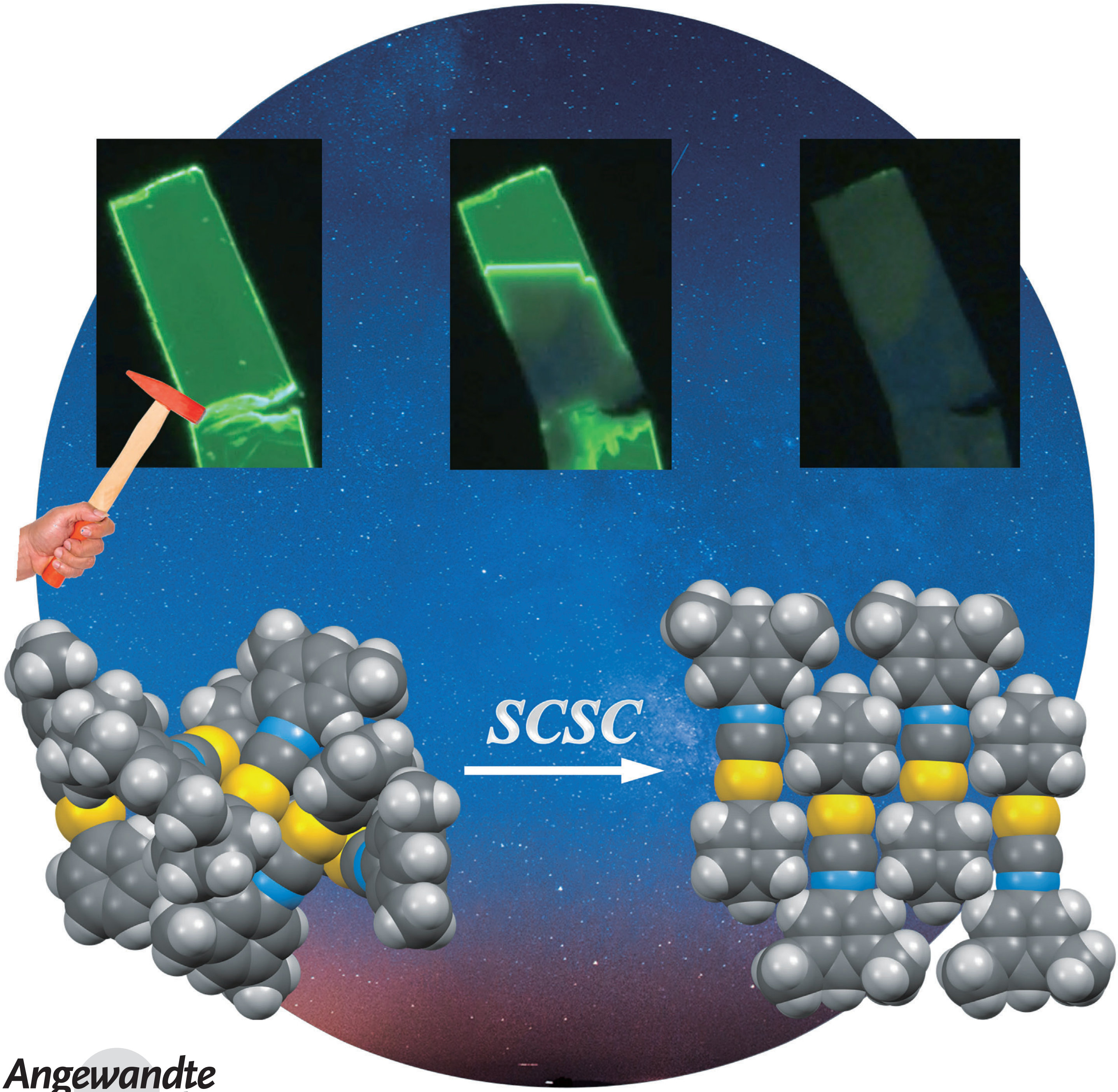

Angewandte International Edition Chemie

Organic and organometallic materials with mechano-responsive properties have been intensively studied because these materials can potentially be used in various applications such as photodevices, sensors, probes, and memory devices.[1] These responses generally depend on structure alteration upon a mechanical stimulus.[2] The most important but still unexplored feature of these materials is an explanation of how the mechanical force at the bulk scale affects the molecular structure. Additionally, it is desirable to develop a new material using detailed structure information obtained from the mechano-responsive behavior.

Over the past few years our group has been interested in the luminescence mechanochromism of gold(I) complexes.[3] We recently discovered a novel phenomenon with regard to this subject (Figure 1): A small mechanical stimulation on the local area of the metastable polymorph crystal I of phenyl(phenyl isocyanide)gold **1** can trigger a phase transition to the thermodynamically stable phase II (Figure 1).[3b] The phase conversion gradually spreads throughout the entire crystal (Figure 1 a). A significant red-shift in the photoluminescence spectrum was also observed under UV irradiation. This phase transformation proceeds in a single-crystal-to-single-crystal (SCSC) manner. X-ray diffraction analysis of single crystals is the most powerful method for detailed studies on crystalline structures; however, a SCSC phase transition has never been reported in any study about mechano-responsive materials.[4–8] This may be because the application of force stimulation to the crystals tends to cause significant damage to the crystals making this powerful technique unusable. Our previous result was the first reported SCSC phase transition of mechano-responsive materials.[3b] Single-crystal X-ray analyses of both crystals gave detailed structural information, and we could thus infer that this photoluminescence change is due to the largely different crystalline structures of I and II. Crystal I is a metastable polymorph possessing a herringbone-like structure with CH/π interactions, whereas in the thermodynamically stable structure II, significant aurophilic bonds, which account for the red-shifted luminescence, were formed through the SCSC phase transition (Figure 1 b). The SCSC phase transition was also promoted by contact between seed crystal II and crystal I.[3b]

These preliminary results gave us valuable information about the molecular structure and prompted us to develop a new mechanically triggered material with a different change profile with regard to structure and optical response. We report here a semi-rational molecular design of the mechanically induced and seeding-triggered SCSC phase transition and focus on the disconnection of aurophilic bonds. Aurophilic bonds have a relatively strong binding energy similar to that of a hydrogen bond and they often cause red-shifted emission in gold complexes.[9] We anticipated that the introduction of substituents that can contribute additional intermolecular interactions to the basic structure **1** would result in a new phase that is thermodynamically more stable than the phase with aurophilic bonds, thus enabling the disconnection of aurophilic bonds through a SCSC phase transition (Figure 1 b). As a proof-of-principle, we conducted an extensive investigation and found that phenyl(3,5-dimethylphenyl isocyanide)gold(I) (**2**), in which two methyl groups are introduced into the basic structure **1**, shows a mechanically induced and seeding-triggered SCSC phase transition. Remarkably, for the SCSC phase transition of complex **2**, changes in the profile of the crystal structures and emission energy are opposite to those found for the basic complex **1** (Figure 1 b). The green emissive metastable phase I of complex **2**, including the intermolecular aurophilic interactions in the crystal structure, underwent a picking-triggered SCSC phase transition to afford the blue-shifted, weakly blue emissive phase II, which possesses multiple CH/π interactions without aurophilic interactions. The formation of multiple CH/π interactions including the added methyl groups of **2** caused the emergence of the thermodynamically stable phase II and it had an opposite SCSC phase transition profile to that of **1**.

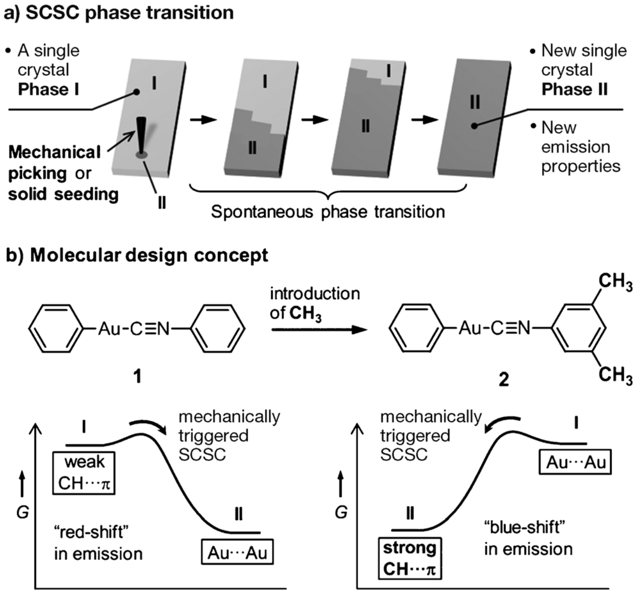

Figure 1. a) Single-crystal-to-single-crystal (SCSC) phase transition triggered by mechanical picking, which is accompanied by a photoluminescence color change. b) Chemical structures and conceptual diagrams of the SCSC phase transition of **1** and **2** (G = free-energy).

The SCSC phase transition of the green-emissive polymorph of **2** (**2g**) to the new phase **2b** was triggered by mechanical picking as shown in Figure 2 (see also the movie S1 in the Supporting Information). Crystals of **2g** showed green photoluminescence at UV irradiation (Fig-

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[**] This work was financially supported by the Funding Program for Next Generation World-Leading Researchers (NEXT Program, No. G002) from the Japan Society for the Promotion of Science (JSPS) and the MEXT (Japan) program "Strategic Molecular and Materials Chemistry through Innovative Coupling Reactions" of Hokkaido University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307672.

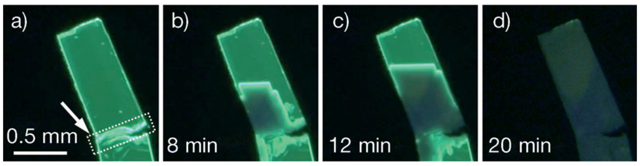

Figure 2. Series of photographs showing the mechanically triggered SCSC phase transition from a) **2g** to d) **2b**. The photographs were taken under ambient conditions and at 365 nm illumination. The arrow indicates the area where the mechanical stimulus was applied.

ure 2 a) and they were obtained by the crystallization of **2** from CH_2Cl_2/hexane for 3 h. A small mechanical stimulus was applied to the single crystal of **2g** with a needle (white arrow in Figure 2 a). A phase change of the starting small domain was observed around the picking area, and it showed a reduced emission intensity that was blue. Remarkably, the initially formed local crystalline domains with blue emission spontaneously expanded under ambient conditions without further application of external stimuli, as shown in Figure 2 b–d. Within 20 minutes the entire crystal showed pale-blue emission (Figure 2 d). The crystal sample obtained after the mechanically triggered transformation had enough quality for X-ray single-crystal analysis, which confirmed the SCSC phase transition of **2g** to **2b**. The rate of the SCSC phase transition of **2** depends on the crystals and the process is typically complete in less than 30 minutes.

The emission properties of the pristine single crystal **2g** were investigated in detail. The emission spectrum of **2g** was obtained upon excitation at 310 nm and exhibited an emission maximum at 535 nm (black solid line in Figure 3). The excitation spectrum was detected at 535 nm and showed a structureless broad band around 250–450 nm (black dotted line in Figure 3). The absolute quantum yield Φ_{em} of photoluminescence ($\lambda_{ex} = 310$ nm) was very high (0.84). The average emission lifetime (τ_{av}) was determined to be 0.97 μs (Figure S1 and Table S1). Photoluminescence was hardly observed for the molecularly dissolved states of **2** in CH_2Cl_2 ($\Phi_{em} = 0.028$; Figures S2 and S3 and Table S1), indicating that the emission properties of **2g** rely heavily on the crystal structure.

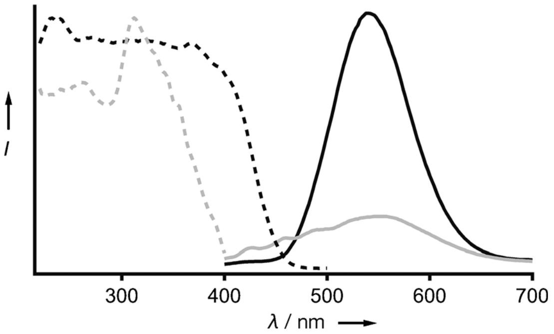

Figure 3. Excitation spectra of **2g** (black dotted line, detected at 535 nm) and **2b** (gray dotted line, detected at 445 nm) normalized with their maximum intensities and emission spectra of **2g** (black solid line) and **2b** (gray solid line) normalized with the corresponding maximum absorption intensities ($\lambda_{ex} = 310$ nm).

Spectroscopic studies showed that the optical properties were significantly altered upon the SCSC phase transition from **2g** to **2b**. The emission spectra of **2b** at 310 nm excitation revealed that the broad emission band with a maximum at 555 nm (gray solid line in Figure 3) had an intensity of about one fifth that of **2g** when normalized based on the maximum absorption intensities of these two polymorphs. The Φ_{em} value of **2b** is also low at 0.06 (Table S1). In addition to the "green" emission band at 555 nm, **2b** exhibited a new emission band at 400–460 nm with lower intensity. This emerging emission band is derived from the newly formed crystalline structure that was generated upon the SCSC phase transition. The residual "green" emission band at 555 nm for **2b** disappeared upon thermal annealing (Figure S4). This indicates that the "green" emission band of **2b** originates from the remaining traces of the thermodynamically less stable **2g** domains.[10]

Molecular arrangements in the **2g** crystals were investigated by single-crystal X-ray analysis. Single crystals with satisfactory accuracy were reproducibly obtained (e.g. $R_1 = 0.0912$, $wR_2 = 0.2295$, $GOF = 1.030$, Table S2). X-ray analysis, elemental analysis, thermal gravimetric analysis (TGA) and ^{1}H NMR measurement revealed that there is no solvent inclusion (Tables S2 and S3, Figure S5, S7, and S8). Compound **2g** crystallized in the monoclinic space group $P2_1/n$ with a relatively large unit cell ($Z = 24$, $V = 8330$ Å^3). The molecules had a distorted conformation with intramolecular dihedral angles between the phenyl and dimethylphenyl rings ranging from 13.04 to 66.00°. One unique feature of **2g** would be the hexamers that were bound together through intermolecular aurophilic interactions[5] with the longest Au–Au distance between adjacent molecules being less than 3.274 Å (Figure 4 a). The hexamers further associate with adjacent hexamers by π–π stacking interactions at the terminal dimethylphenyl moieties to form extended one-dimensional columnar-like aggregates (Figure 4 b and c). All

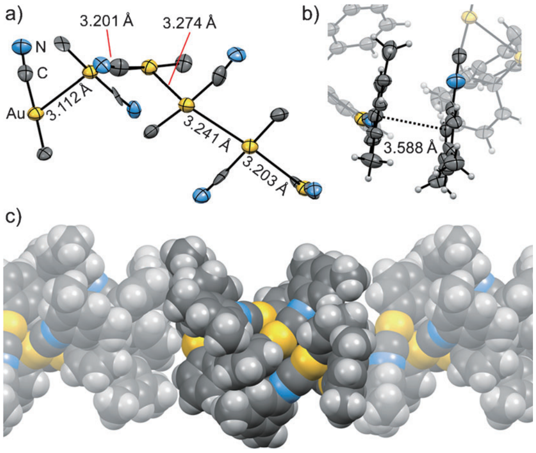

Figure 4. Single-crystal X-ray analysis of **2g**. a) Hexamer unit bound through multiple intermolecular aurophilic interactions with Au–Au distances ranging from 3.112 to 3.274 Å. Phenyl groups except for one carbon atom and dimethylphenyl moieties are omitted for clarity. b) π–π Stacking interactions between two hexamer units at the terminal dimethylphenyl moieties. c) One-dimensional columnar aggregates extended through multiple π–π stacking interactions.

the adjacent columns run parallel to the *b* axis and interact laterally. The crystalline lattice possesses an empty void between the columns and composes 5.2% of the crystal volume (Figure S8).

A single-crystal X-ray analysis of **2b** that formed upon the mechanically triggered SCSC phase transition of **2g** was successfully conducted with satisfactory accuracy ($R_1 = 0.0783$, $wR_2 = 0.1171$, $GOF = 1.007$). The crystal structure of **2b** was largely different from that of the precursor crystal **2g**. Polymorph **2b** crystallized into the orthorhombic space group *Ima*2 (Table S2). All the molecules in the lattice showed rotational disorder at the phenyl and the dimethylphenyl rings with intramolecular dihedral angles of 52.61°. Their molecular long axis was oriented along the *b* axis (Figure 5a and b) and the molecules were packed without an empty void region. Each molecule of **2b** forms four CH/π interactions as the two CH moieties from both the methyl groups and the two π moieties from both faces of the phenyl groups with intermolecular CH-to-π distances ranging from 2.910 to 3.057 Å (the central molecule in Figure 5c). In contrast, the shortest intermolecular Au–Au distance was 4.784 Å indicating the absence of aurophilic interactions. The absence of solvent molecules within the lattice of **2b** was again clearly confirmed (Tables S2 and S3, Figure S6 and S7). These X-ray analyses of **2g** and **2b** revealed that the structure alternation causes the emission color change. Time-dependent density functional theory (TDDFT) calculations based on the structures of **2g** and **2b** indicate that the blue shift of the emission upon the SCSC phase transition can be attributed to the disconnection of aurophilic interactions (Figure S9).

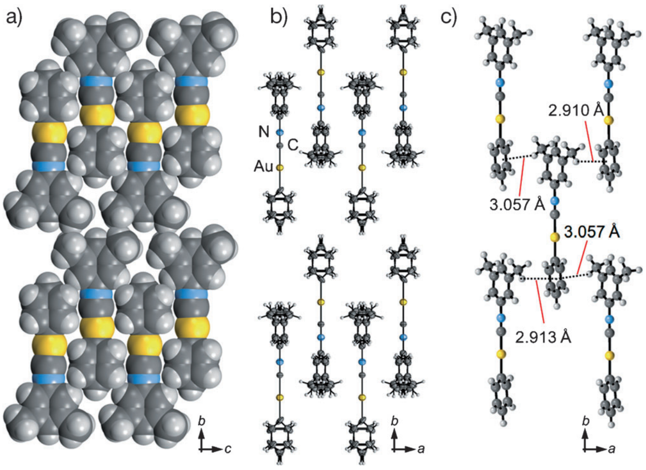

Figure 5. a) Space-filling representation for single crystals of **2b** viewed along the *a* axis. b) ORTEP representations with thermal ellipsoids at 50% probability for single crystals of **2b** viewed along the *c* axis. The phenyl and dimethyl phenyl moieties in **2b** are rotationally disordered over two sites with 50% probability. c) Pentamer derived from the single-crystal structures of **2b** shown by a ball-and-stick representation with four intermolecular CH/π interactions of the central molecule. One set of the groups exhibiting disorder is omitted for clarity.

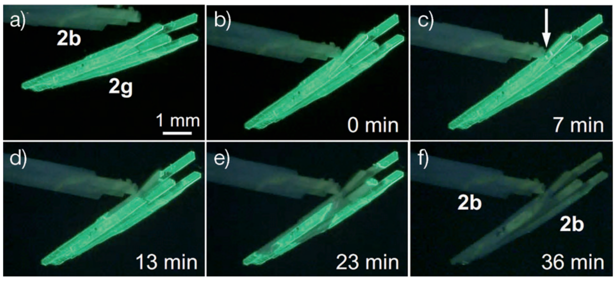

Figure 6. Series of photographs for the solid seeding-triggered SCSC phase transition from **2g** to **2b**. The photographs were obtained from movie S2, which were taken under ambient conditions at 365 nm illumination. The arrow in (c) indicates the contact area between the two crystals where initial phase change was observed.

Contacting the seed crystal of **2b** with **2g** crystals can also induce the SCSC phase transition, as shown in Figure 6 and in movie S2. When a "seed" crystal of **2b** was obtained after the mechanically triggered SCSC phase transition and was gently attached to the **2g** crystal with tweezers (Figure 6a and b), the phase change from **2g** to **2b** was initiated at the contact area at room temperature (arrow in Figure 6c). The phase change took place in the crystal without applying additional stimuli and it propagated through contact with the surface of the neighboring crystals (Figure 6d–f). The phase transformation was complete over the entire solid sample after 36 minutes (Figure 6f). After the completion of the phase change we conducted X-ray diffraction analysis of a single crystal that was cut from the sample to confirm that the phase change occurred in a SCSC manner in each crystal and that the crystal structure is identical to that of the mechanically induced **2b**. A phase change of **2g** was not induced by gentle attachment of other objects such as tweezers instead of the attachment of the crystals **2b**. To our knowledge, there have been no reports about solid seeding-triggered SCSC phase transition other than our previous study on **1**.[3b]

The SCSC phase transition to **2b** can also be performed upon heating the pristine single crystal **2g**. DSC analysis showed the phase transition and melting temperature of **2g** are 42 and 102 °C, respectively (data not shown). We thus heated the pristine single crystal **2g** at 40 °C for 10 minutes. The resulting crystal is also well-suited for single-crystal X-ray analysis (Table S2). The packing structure of the thermally treated crystals is identical to those of the mechanically treated crystals **2b** (Table S2). This result shows the superior thermodynamic stability of the polymorphs obtained after the SCSC phase transition. The blue-emissive polymorphs of complex **2** can be directly prepared from the solution phase when the crystallization of **2** is performed slowly (e.g. 12 h). In general, kinetically isolated polymorphs are crystallized under rapid crystallization conditions, whereas thermodynamically favored polymorphs are formed under slow crystallization conditions. This is known as Ostwald's step rule and often occurs in solution-phase crystallization.[11] For complex **2**, the phase transition occurred because of the formation of multiple CH/π interactions and the loss of void regions compensates for the energy loss from the disconnection of intermolecular aurophilic bonds.

Here we report that the SCSC phase transition from **2g** to **2b** can be triggered by small mechanical picking and solid seeding. Single-crystal X-ray analyses of **2g** and **2b** showed that the crystalline structure changed drastically and, in particular, the aurophilic interactions were lost upon the SCSC phase transition, which resulted in blue-shifted photoluminescence. These changing profiles are complementary to the basic complex **1**; we have successfully demonstrated the new aspects of the remarkable SCSC phase-transition phenomena by introducing methyl groups to the basic molecular structure of **1**. Further development of other derivatives displaying the SCSC phase transition and the investigation of the phase transformation mechanism at molecular level are currently underway.

Received: August 31, 2013

Keywords: aurophilic interactions · emission · luminescence · phase transitions · polymorphism · single crystals

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[10] The amount of remaining original crystalline domain **2g** embedded within single crystal **2b** must be small so as not to affect the single-crystal X-ray analysis (Table S2). Emission from trace amounts of the crystalline domain of **2g** within **2b** is discernible likely because of the high Φ_{em} of 0.84 and the presence of energy transfer events to **2g** with a low-excitation energy level.

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