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Advance Publication on the web June 23, 2017 doi:10.1246/cl.170482

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## Tuning the Lifetime of Transient Phases of Mechanochromic Gold Isocyanide Complexes through Functionalization of the Terminal Moieties of Flexible Side Chains

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The lifetime of the transient phases of luminescent mechanochromic gold isocyanide complexes could be tuned through the modification of termini of flexible side chains. Upon grinding, these complexes initially showed an emission color change from blue to yellow. The yellow emission spontaneously changed to blue or green but with different lifetime of the yellow-emitting transient phases depending on the substituents. Details of the mechano-induced structure changes were also described.

When solid-state emission colors of organic or inorganic compounds changes upon grinding ( $C \rightarrow G$ , Figure 1a), such a phenomenon is called luminescent mechanochromism (hereafter, referred to as "mechanochromism").<sup>1</sup> Mechanochromic compounds are promising as sensors and memory devices.<sup>2</sup> Emission color changes of mechanochromic compounds generally originate from molecular rearrangement induced by mechanical stimulation.<sup>3</sup> In most cases, intermolecular interactions that influence emission properties are changed, which induces emission color changes.<sup>1,4</sup> Once formed, the ground phases are generally stable under ambient conditions for a long period (Figure 1a) because no further molecular rearrangement occurs.





**Figure 1.** Schematic representations of a) typical mechanochromism and b) mechanochromism involving a transient phase.

We have intensively studied the luminescent mechanochromism of a series of aryl gold isocyanide complexes.<sup>5,6</sup> These aryl gold isocyanide complexes are highly sensitive to mechanical stimulation and their subtle structural modification often leads to remarkable alteration

of their mechanochromic properties.<sup>5,6</sup> Interestingly, complex 1 possessing flexible tetraethylene glycol (TEG) side chains (Figure 2) exhibited unprecedented mechanochromism: upon mechanical stimulation, a blue-emitting pristine sample of 1 (1B) initially formed a yellow-emitting transient phase 1Y before spontaneously transforming to green-emitting phase 1G over 2 s (Figure 2). X-ray diffraction (XRD) analysis revealed that 1B and 1G are two different crystalline phases and both have alternating layer structures composed of rigid luminophoric sublayers and flexible TEG sublayers. In contrast, 1Y was found to be amorphous phase. Although more than ten mechanochromic compounds that spontaneously recover the original phase from their ground "transient" phases have been reported (i.e.,  $C_1 \rightarrow [T] \rightarrow C_1$ , Figure 1b)<sup>8</sup>, 1 was the first mechanochromic compound that exhibits crystal-to-crystal phase transition mediated by a short-lived "transient" phase  $(C_1 \rightarrow [T] \rightarrow C_2$ , Figure 1b).



Figure 2. Structures and photographs of powder samples of 1, 2, and 3 taken under UV illumination.

Here, we tune the lifetime of transient phases of gold isocyanide complexes through functionalization of the terminal groups of their flexible TEG side chains. We prepared new compounds 2 and 3 possessing rigid tolyl (2) and flexible hexyl groups (3). Both 2 and 3 show mechanochromism involving short-lived transient phases. The transient phase of 2 spontaneously transforms into a new phase (similar to 1), whereas that of 3 transforms into the original phase (self-recovery). The lifetimes of the transient phases of 1, 2, and 3 are evaluated by emission spectroscopy, and the crystal structures of **2** and **3** are analyzed by XRD to elucidate the mechanism of the transient mechanochromism.

New complexes 2 and 3 were prepared according to a modified reported procedure.<sup>7</sup> Reprecipitation of 2 in  $CH_2Cl_2$  and MeOH (or hexane) gave white powder 2B exhibiting blue emission under UV illumination. Similarly, blue-emitting 3 (3B) was obtained through a similar reprecipitation procedure. NMR spectra of 2B and 3B in  $CDCl_3$  indicate that the powder samples do not contain solvent molecules (Figure S1).

Complexes 2 and 3 showed mechanochromism mediated by transient phases. Upon grinding blue-emitting 2B, its emission color initially changed to yellow because of the formation of 2Y (Figure 2). Under ambient conditions, the emission color of 2Y spontaneously transformed to green over 150 s because of the formation of 2G (Figure 2). This observation demonstrates that 2 displays mechanochromism including the transient **2Y** phase similar to **1**; i.e.,  $C_1 \rightarrow [T]$  $\rightarrow$  C<sub>2</sub> (Figure 1b). The mechanochromism of **2** was evaluated by steady-state and time-resolved emission spectroscopy (Figure 3a). Upon excitation at 365 nm, 2B exhibited a broad emission spectrum with an emission maximum wavelength  $\lambda_{em,max}$  of 472 nm (blue line in Figure 3a). The absolute emission quantum yield  $\Phi_{\rm em}$  and average emission lifetime  $\tau_{av}^{9}$  of **2B** are 0.095 and 42.7 µs, respectively (Figure S2 and Table S1). Upon grinding **2B**, a bathochromic shift was initially observed and the resulting **2Y** has  $\lambda_{em,max} = 538$  nm (yellow line in Figure 3a). Upon standing **2Y** under ambient conditions, a gradual hypsochromic shift was observed over 150 s (yellow to green lines in Figure 3a).  $\lambda_{em,max}$  of 2G is 522 nm and  $\Phi_{em}$  is 0.14, and  $\tau_{av}$  is 18.1 µs (Figure S2 and Table S1). These spectral features are similar to those of 1.

For complex 3, mechanical stimulation of blue-emitting pristine phase 3B initially afforded yellow-emitting phase 3Y (Figure 2). This transient phase 3Y immediately transformed to blue-emitting 3B' (< 1 s, Figure 2). Emission spectra of 3B and 3B' showed similar structured emission bands with peaks at 447 and 466 nm (Figure 3b; see Table S1 for photophysical properties). The spectral similarity implies the self-recovery of the original phase from the transient phase 3Y; i.e.,  $C_1 \rightarrow [T] \rightarrow C_1$  (Figure 1b). The emission spectrum of 3Y could not be detected because of its short lifetime. For 2B and 3B, increasing temperature causes emission color changes at 125 and 85 °C, respectively, different from those induced by mechanical stimulation, probably because of chemical decomposition.



Figure 3. Emission spectra of a) 2 and b) 3 upon mechanical stimulation. Excitation wavelength = 365 nm. The red arrow in a) indicates the spectral changes during the spontaneous phase transition.

To investigate the mechanism of mechanochromism of 2 and 3, powder XRD measurements were conducted. The pristine powder of 2B exhibited a diffraction pattern featuring many intense peaks (Figure S3), indicating its crystalline nature. Ground powder 2G was also found to be crystalline powder from its XRD pattern (Figure S3). Importantly, the peak position of the diffraction pattern of 2G is different from that of 2B. This clearly indicates that the molecular arrangements of 2B and 2G are different from each other, excluding the possibility of the self-recovery from the transient phase **2Y**; i.e.,  $C_1 \rightarrow [T] \rightarrow C_2$  (Figure 1b). Although the powder XRD pattern of short-lived 2Y could not be measured in this study, 2Y has molecular arrangements different from those of 2B and 2G considering the previously reported result of 1 whose yellow-emitting transient phase has proven an amorphous phase.7,10 For complex 3, we compared the powder XRD patterns of 3B and 3B'. Unground 3B and ground 3B' gave almost identical diffraction patterns (Figure S3), which indicates that they are crystalline phases with essentially the same molecular arrangements. Accordingly, the blue-emitting original phase must be recovered from the transient phase 2Y,<sup>11</sup> which is in line with the results of emission spectroscopy  $(C_1 \rightarrow [T] \rightarrow$  $C_1$ , Figure 1b).

We next evaluated the lifetimes of the transient phases of 1–3 at room temperature by probing emission intensity. As mentioned above, 1Y, 2Y, and 3Y are short-lived transient intermediates that spontaneously transform to different phases with different time ranges (Figure 2). To evaluate their lifetimes, emission intensities at the  $\lambda_{em,max}$  of 1Y, 2Y, and 3Y were plotted as a function of time just after mechanical stimulation (Figure 4). The emission intensity of 1 decreased abruptly after mechanical simulation, indicating the rapid transformation of 1Y into 1G after mechanical stimulation ceased. Conversely, 2Y took 100 s to make its emission intensity half, indicating the longer lifetime of the transient phase 2Y. The emission spectrum of 3Y could not be detected because of the very rapid transformation of 3Y into 3B' (lifetime: < 1 s).



Figure 4. Decay profiles for the intermediate species monitored by emission intensity at 564 nm for 1 (circles) and 538 nm for 2 (squares). Inset shows a magnified view of the short time range.



Figure 5. Single-crystal structures and photographs (insets, taken under UV light) of 2B (a-c) and 2G (d-f).

The different lifetimes of the transient phases **1Y**, **2Y**, and **3Y** can be rationalized by considering the character of the terminal substituents on their side chains. On one hand, the tolyl group of **2** can form stronger intermolecular interactions compared to a methyl group of **1** due to effective  $\pi$ - $\pi$  stacking. Such  $\pi$ - $\pi$  stacking formed in the transient **2Y** phase possibly could slow the reorganization of the molecular arrangement. On the other hand, the side chains of **3** do not have such aromatic groups. Upon grinding **3B**, a subtle reorganization of molecules takes place to form yellow-emitting **3Y**, which cannot be effectively stabilized by interactions between side chains. As a result, the rapid self-recovery of **3B** may occur.

We successfully grew two single crystals of 2 corresponding to 2B and 2G (Figure 5). A blue-emitting single crystal of 2 was prepared from CH<sub>2</sub>Cl<sub>2</sub>/hexane at room temperature and crystallized in triclinic space group P-1 (Table S2). From this single-crystal pattern, a simulated powder XRD pattern was generated that was consistent with the powder XRD pattern of 2B (Figure S4). The central luminophore moiety has a flat conformation: the dihedral angle between an isocyanide benzene ring and tetrafluorobenzene rings on Au ( $\theta_d$ ) is 3.22° (Figure 5a). In addition, the entire molecules including flexible TEG segments adopt a rather straight conformation (Figure 5a). Together with two neighboring molecules, each molecule in 2B forms two aurophilic interactions with an Au…Au distance of 3.2666(4) Å (red dotted lines in Figure 5b),<sup>6,12</sup> forming open-ended polymeric chains. The molecular packing of previously reported  $\mathbf{1}^7$  features alternating layers consisting of rigid luminophore sublayers and flexible TEG sublayers (vida supra). However, the molecular packing of 2B does not contain such a segregated layer-by-layer

arrangement (Figure 5c). A green-emitting single crystal of 2G was prepared from acetone at -25 °C and crystallized in monoclinic space group  $P2_1/c$  (Table S2). The luminophore segments of 2G adopt a conformation that slightly deviates from the perpendicular alignment, with  $\theta_d = 19.39^\circ$  (Figure 5d). Molecules in 2G adopt an S-shaped conformation, taking advantage of the flexible TEG moieties (Figure 5d).<sup>13</sup> The intermolecular nearest Au…Au distance of 2G is 5.3253(4) Å, indicating there are no aurophilic interactions. However, two-fold Au $\cdots \pi$  interactions (3.378 Å, red dotted lines) are observed with a neighboring molecule, forming open-ended polymeric chains (Figure 5e).14 In addition, an alternating layer structure containing rigid gold isocyanide sublayers and flexible TEG layers is formed (Figure 5f), similar to previously reported **1B** and **1G**.<sup>7</sup> It is supposed that the large difference of the molecular packing of 2B and 2G (Figure 5) also contributes to the long lifetime of **2Y**.

A blue-emitting single crystal of **3** was also obtained by repeated recrystallization (Figure 6). Recrystallization of **3** from a CH<sub>2</sub>Cl<sub>2</sub>/MeOH mixture at -25 °C afforded the blue-emitting single crystal. The experimentally obtained powder XRD pattern of **3B** was completely reproduced from the resulting single crystal of **3** (Figure S4). The single crystal of **3B** crystallized in triclinic space group *P*-1 (Table S2). The central gold isocyanide moiety has a twisted conformation with  $\theta_d = 80.62^\circ$ . The molecules in **3B** adopt a straight conformation similar to those in **2B**; however, the terminal hexyl groups exhibit disorder (Figure 6a). Molecules form two-fold Au… $\pi$  interactions (3.403 Å, red dotted lines in Figure 6b) with neighboring molecules to construct polymeric chains. The nearest Au…Au distance is 5.4166(8) Å, indicating there are no aurophilic interactions.



Figure 6. Single-crystal structure of **3B**. A set of disordered segments of hexyl moieties is highlighted in light blue.

In summary, the lifetimes of the transient phases of aryl gold isocvanide complexes could be tuned by modifying the terminal structure of the TEG side chains. The new complexes 2 and 3 possessing tolyl and hexyl groups, respectively, at the side chain termini, showed unique mechanochromism involving transient amorphous phases. Furthermore, the lifetimes of the transient phases depend on the structure of side chain termini: the rigid tolyl groups slowed the spontaneous phase transition of 2, while the flexible hexyl groups facilitated the spontaneous phase transition of 3. XRD analyses also provided detailed structural information about 2 and 3, and the markedly different molecular arrangements in 2 upon grinding reflect the slow reorganization from the transient 2Y phase. This work provides new insights into the structure-property relationship of a unique class of mechanochromic gold complexes.

Supporting	Information	is	available	on
http://dx.doi.or	g/10.1246/cl.****	***.		

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- [11] The molecular arrangement of **3Y** has not been determined yet.
- [12] Previously reported blue-emitting **1B** exhibited aurophilic interactions: see reference 7.
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