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Luminescent mechanochromism of gold *N*-heterocyclic carbene complexes with hypso- and bathochromic spectral shifts

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Two gold *N*-heterocyclic carbene complexes show contrasting luminescent mechanochromism behavior with hypso- and bathochromic spectral shifts. The distinct emission shifts upon mechanical stimulation can be explained by the aggregate-to-monomer transformation and intensified intermolecular interactions, respectively.

Luminescent mechanochromism is a topic of current interest owing to its possible applications in sensing and recording devices.¹ Many groups have reported luminescent mechanochromism in a variety of organic² and organometallic³ compounds, as well as polymeric materials.⁴ The origin of the emission color changes is typically based on the molecular arrangement changes after mechanical stimulation. Mostly, the intermolecular interactions of this class of compounds are intensified in the ground phases, which often lead to a bathochromic emission spectral shift.¹

Our group has focused on the luminescent mechanochromic properties of a series of gold isocyanide complexes.^{3,5} Various mechanochromic gold isocyanide complexes that show single-crystal-to-single-crystal phase transitions,^{5b,c} multiple-color emission,^{5d} infrared emission,^{5e} and noncentrosymmetric-to-centrosymmetric phase transitions^{5f} have been reported. Our previous studies have established a library of gold isocyanide complexes as stimuli-responsive luminescent solid compounds.^{3,5b-f} Recently, we turned our attention to investigation of a group of gold *N*-heterocyclic carbene (NHC) complexes to develop a new series of stimuli-responsive solid materials including mechanochromic materials. NHC compounds tend to act as stable ligands for gold complexes similar to isocyanides, but their topologies and electronic states

are different.⁶ Thus, gold NHC complexes could show different stimuli responsivity to gold isocyanide complexes. Gold NHC complexes have been reported by several groups, and their solid-state emission properties have been investigated.⁷ However, their luminescent mechanochromic properties have rarely been reported.⁸ Most NHC complexes show simple bathochromic emission spectral shifts upon grinding.⁹ We have recently prepared various gold complexes having NHC ligands with fused aromatic rings to ensure their emissive nature. As a result, we found two mechanochromic NHC gold complexes with hypso- and bathochromic shifts with distinct structure alternation mechanisms of CH/ π aggregation to isolation and CH/ π aggregation to π - π stacking formation, respectively.

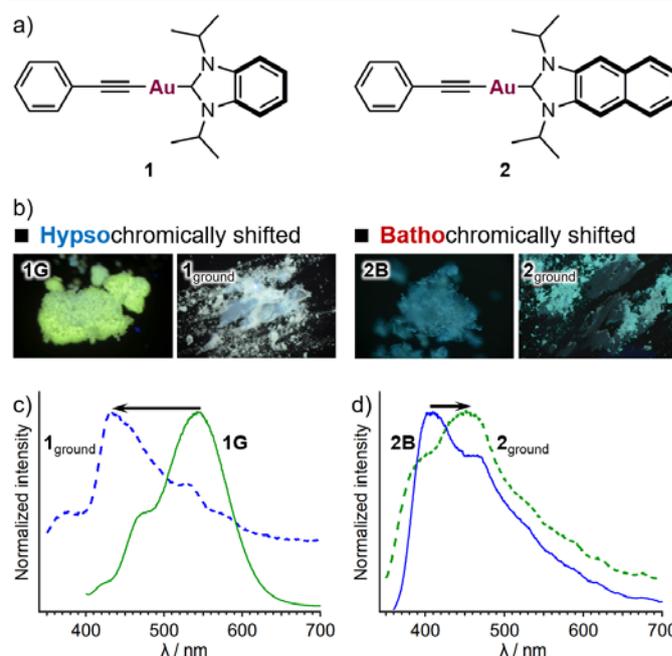


Fig. 1 (a) Structures of **1** and **2**. (b) Photographs of **1** and **2** obtained before and after mechanical stimulation taken under UV light. Emission spectra of (c) **1G** (green line) and **1G_{ground}** (blue dashed line) and (d) **2B** (blue line) and **2B_{ground}** (green dashed line) under

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excitation at 365 nm. The arrows in (c) and (d) indicate the changes upon mechanical stimulation.

Here, we report the mechanochromic luminescent properties of **1** and newly prepared analogue **2** (Fig. 1). Both complexes show clear emission color changes upon grinding. Complex **1** shows hypsochromically shifted emission from green to blue after mechanical stimulation, whereas the emission of complex **2** exhibits a bathochromic shift and a blue-to-green emission color change occurs. X-ray diffraction (XRD) measurements indicate that both complexes undergo crystal-to-amorphous phase transitions upon grinding. The detailed mechanisms of the opposite emission spectral shifts of **1** and **2** will be discussed. Venkatesan and co-workers^{7b} reported the crystal structure and luminescent properties of complex **1** (Fig. 1), but they did not report its luminescent mechanochromic properties.

Synthesis of **1**^{7b} and **2** was performed according to the procedures described in the ESI. After purification, **1** was obtained as a white solid (Fig. S1). Under UV illumination at 365 nm, the resulting crystals show green emission with high absolute emission quantum yield (Φ_{em}) of 34.0% and are called **1G** (Fig. 1b). For **2**, purification of this complex by column chromatography afforded a brownish solid (Fig. S1) that exhibits blue emission with low Φ_{em} (0.26%) by photoexcitation (Fig. 1b). Hereafter, this form is called **2B**.

To determine the mechanochromic luminescent properties of **1** and **2**, we ground **1G** and **2B**. After mechanical stimulation of green-emitting **1G** with a spatula, the resulting powder **1_{ground}** shows blue emission (Φ_{em} = 4.8%, Fig. 1b), confirming clear mechanochromic luminescence. Upon grinding blue-emitting **2B**, the resulting powder **2_{ground}** shows weak green emission (Φ_{em} = 0.32%, Fig. 1b). This observation also reveals the luminescent mechanochromic properties of **2**.

Emission spectroscopy indicates that **1** exhibits a shift to higher energy and **2** exhibits a shift to lower energy upon mechanical stimulation (Fig. 1c and d).¹⁰ Under excitation at 365 nm, **1G** shows a broad emission spectrum with a peak at 544 nm (green line, Fig. 1c). The emission spectrum of **1_{ground}** obtained after mechanical stimulation has a maximum at a shorter wavelength (emission maximum at 431 nm, blue dashed line, Fig. 1c). This confirms the luminescent mechanochromism of **1** with a shift to higher energy. Most luminescent mechanochromic compounds show a bathochromic shift in the emission wavelength by grinding and few mechanochromic compounds showing hypsochromically shifted emission have been reported.¹¹ We confirmed that Φ_{em} decreases (34.0% → 4.8%) and the average emission lifetime τ_{av} shortens (0.90 μ s → 0.77 μ s) upon grinding **1** (Fig. S2 and Table S1). For **2**, the emission spectrum of the unground form **2B** exhibits a maximum at 410 nm (blue line, Fig. 1d). After mechanical stimulation, **2_{ground}** shows a bathochromically shifted emission band with a peak at 453 nm (green line, Fig. 1d).¹² Thus, the directions of the emission spectral shifts of **1** and **2** are opposite.

To investigate the mechanism of the observed luminescent mechanochromism, crystal structure analyses were performed. We first investigated the single-crystal structure of **1** (Figs. 2 and

S3 and Table S2).^{7b} Recrystallization of **1** from CH₂Cl₂ and hexane (see ESI) afforded the single-crystal sample **1G** with green emission. The single-crystal XRD analyses indicate that the structure of **1G** is the same as that previously reported.^{7b,13} **1** crystallizes in the orthorhombic space group *Pbca*. The molecules are slightly bent (Fig. 2a). There are intermolecular CH \cdots π interactions between a H atom of the isopropyl group and the benzene ring of the phenylethynyl group (2.857 Å) or NHC group (2.748 Å) (black dashed lines, Fig. 2c). Although **1** has flat π planes (phenylethynyl and benzoimidazolium groups), there are no clear plane–plane interactions, such as $\pi\cdots\pi$ stacking interactions. This is because of the presence of the bulky isopropyl groups on the N atoms of **1**.

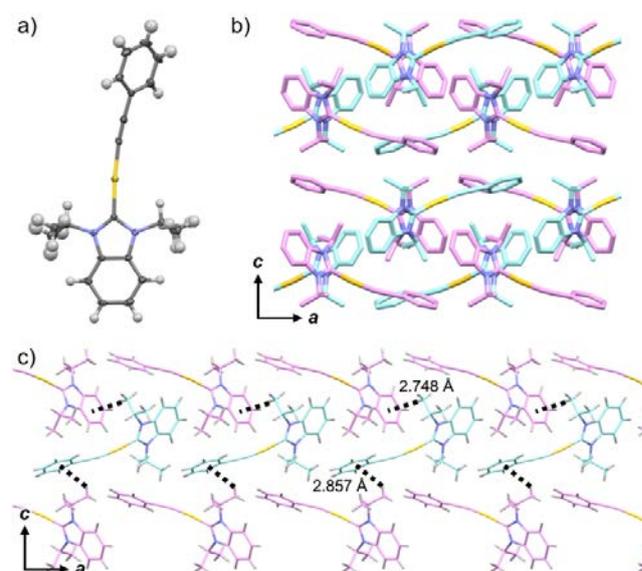


Fig. 2 Single-crystal structure of **1G**.^{7a} (a) ORTEP drawing with 25% probability of a monomer. b,c) Stick representation of the packing arrangements of **1G**.

The single-crystal structure of **2B** was then investigated. The single crystal of **2B** was prepared by recrystallization from CH₂Cl₂ and hexane (see ESI). In **2B**, complex **2** crystallizes in orthorhombic space group *Pnma* with 2 equiv of CH₂Cl₂ in the crystal lattice (Figs. 3 and S4 and Table S2). Differing from **1**, **2** in **2B** has a straight conformation (Fig. 3a). The molecules exhibit disorder at the benzene group. The modeled structure of the benzene moiety is rather complicated (Fig. 3a) because the center of the **2** molecule sits on the mirror plane (Fig. S4). One typical characteristic of **2B** is the perpendicular orientation of the molecules (Fig. 3b and c). Each molecule forms four CH– π interactions with the neighboring four molecules (Fig. 3b). There are two CH– π interactions between the CH groups of this molecule and the NHC or C \equiv C groups of neighboring molecules, as shown by the red dashed lines in Fig. 3b. Two other CH– π interactions form between the NHC or C \equiv C groups of this molecule and the CH groups of neighboring molecules (yellow dashed lines, Fig. 3b). The same molecule interacts with the included CH₂Cl₂ molecules through Cl–H interactions (blue dashed lines, Fig. 3b). Although **2** has two extended flat π planes (Ph–C \equiv C and NHC moieties), face-to-face arrangements (i.e.,

$\pi\cdots\pi$ stacking interactions) are absent in the single-crystal structure of **2B**.

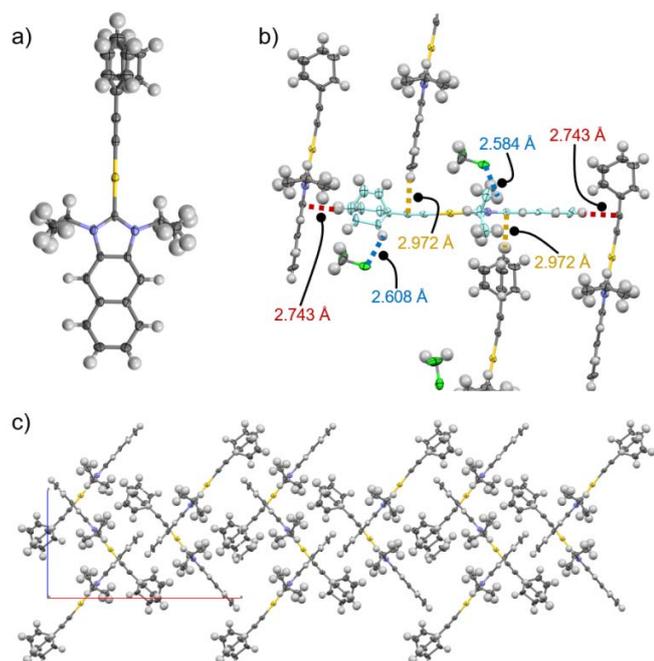


Fig. 3 Single-crystal structure of **2B** in an ORTEP drawing with 25% probability.

Powder XRD (PXRD) measurements indicate that **1** and **2** undergo amorphization by mechanical stimulation (Fig. S5). Comparison of the simulated powder pattern of **1G** derived from the single-crystal structure and the experimentally obtained PXRD pattern of **1_{ground}** indicate that the diffraction peaks of **1_{ground}** disappear after mechanical stimulation (Fig. S5). This indicates that the emission color change of **1** upon grinding occurs because of amorphization. Many mechanochromic compounds show crystal-to-amorphous phase transitions.^{3,5d,e,14,15} Similarly, the intensity of the diffraction peak of **2_{ground}** is weak and no new diffraction peaks are observed after grinding **2B** (Fig. S5). This indicates the crystal-to-amorphous phase transition of **2** upon grinding to express the emission color change.

We then performed emission spectroscopy of **1** and **2** in the solution phase. A solution of **1** in CH_2Cl_2 ($c = 1.3 \times 10^{-6}$ M) shows a structured emission spectrum with a peak at 424 nm (black line, Fig. 4a).^{7b} We confirmed that **1** is in the monomeric state at this concentration by the concentration-dependent UV/vis absorption spectra (Fig. S6). The coverage region of the monomeric emission spectrum of **1** in CH_2Cl_2 almost perfectly matches that of **1_{ground}** accompanied by a similar emission onset (~400 nm) and maximum (~430 nm). This profile is different from that of our previously reported gold isocyanide complexes, in which a clear red-shifted emission band is observed for the solid samples compared with that of the corresponding solution phases. This indicates that the molecules in amorphous phase **1_{ground}** are rather isolated from other molecules to show monomer-like emission. The emission spectrum of the monomeric state of **2** in CH_2Cl_2 ($c = 6.8 \times 10^{-7}$ M)¹⁴ shows peaks at 351 and 394 nm (black line, Fig. 4b). The coverage area of the

monomer emission spectrum of **2** in CH_2Cl_2 is at shorter wavelength and does not match those of the solid states (**2B** and **2_{ground}**, Fig. 4b). This comparison indicates that the solid-state emission of **2** is affected by the intermolecular interactions in the bulk.

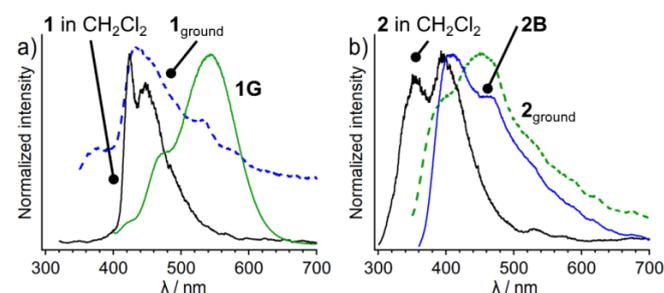


Fig. 4 Emission spectra of solutions of (a) **1** ($c = 1.3 \times 10^{-6}$ M, black line, under excitation at 289 nm) and (b) **2** ($c = 6.8 \times 10^{-7}$ M, black line, under excitation at 244 nm) in CH_2Cl_2 along with the solid-state emission spectra.

The mechanochromism of **1** is based on the aggregate-to-monomer transformation (Fig. 5). The emission spectrum of unground **1G** is located at longer wavelength than that of monomeric **1** in CH_2Cl_2 (Fig. 4). This indicates that the intermolecular interactions (i.e., $\text{CH}\cdots\pi$ interactions) observed in the single-crystal structure of **1G** (Fig. 2) affect the optical properties for long wavelength emission. Upon mechanical stimulation of **1G**, amorphous phase **1_{ground}** forms (Fig. S5). For **1_{ground}**, the similarity between the emission spectra of **1_{ground}** and **1** in CH_2Cl_2 (Fig. 4) suggests that the emission of **1_{ground}** has somewhat monomeric character. The bulky isopropyl groups of **1** prevent effective chromophore–chromophore interactions in the amorphous phase of **1_{ground}**. Similarly, Gierschner et al.¹⁵ reported that rigid π -conjugated molecules equipped with bulky *tert*-butyl groups show monomeric emission in the amorphous solid phase. Several studies of mechanochromic compounds claim that the grinding-induced blue-shifted emission is caused by isolation of molecules with decreased intermolecular interactions after the grinding-induced phase transition.^{11c}

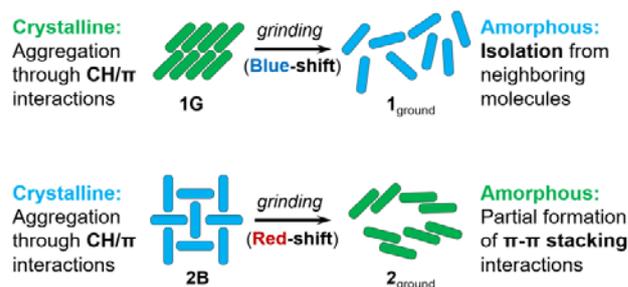


Fig. 5 Schematic representation of the molecular packing of **1** and **2**, which explains the opposite shift of their luminescent mechanochromism.

For **2**, the mechanism of the luminescent mechanochromism is based on the increased intermolecular interactions by grinding (Fig. 5). This is a common mechanism for mechanochromic compounds^{3,5b,e} and different from that of **1**. Comparison of the emission spectra of **2B** and **2** in CH_2Cl_2 (Fig. 4) indicates that in **2B**, intermolecular interactions with the

neighboring molecules (Fig. 3) induce the red-shifted emission compared with the monomeric state of **2**. The single-crystal structure of **2B** shows multiple CH– π interactions to form perpendicularly arranged packing (Fig. 3b and c). After grinding, amorphous **2_{ground}** appears and forms intermolecular interactions in such a way to show bathochromically shifted emission compared with that of **2B**. The degree of CH– π (face-to-edge) interactions in pristine **2B** (Fig. 3) decreases in amorphous **2_{ground}** and the degree of π – π stacking (face-to-face) interactions around the NHC moieties increases (Fig. 5). Although **2** has bulky isopropyl groups as in **1**, the larger π -plane of the NHC group of **2** than that of **1** facilitates the π – π stacking interactions in amorphous **2_{ground}**. Thus, the change in the mode of the intermolecular interactions is the key for the contrasting emission shifts in the mechanochromism of **1** and **2**.

Summary

We have described the luminescent mechanochromism of **1** and **2**, which show hypso- and bathochromic shifts in emission by mechanical stimulation. XRD measurements indicate that both **1** and **2** exhibit a phase transition from the crystalline phase (mainly based on CH– π interactions) to the amorphous phase. For both complexes, comparison of the emission spectra of the solid and solution phases indicates the origin of the contrasting emission spectra shifts. For **1**, isolation of the individual chromophores occurs after grinding to show a blue-shifted emission band, whereas for **2**, the intermolecular interactions are enhanced upon grinding for red-shifted emission. Further investigation of NHC gold complexes to explore their novel functionality is underway.

Acknowledgments

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9. In Ref. 8b, the mechanochromic emission color change is based on an emission intensity decrease of one of two emission bands (a longer wavelength band) rather than a peak shift.
10. The emission mechanism of **1** is reported previously and the mixed characters of a π/π^* (at the phenylethynyl moiety) and a ligand-to-ligand charge transfers (from phenylethynyl to the NHC group) for its emission were suggested: see ref 7b.
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12. Upon grinding of **2**, the increased Φ_{em} and elongated τ_{av} were observed (Fig. S2). Fluorescence nature of **2** is also confirmed.
13. The CCDC number for the previously reported single-crystal data of **1G** is 855992.
14. Thermogravimetric analyses indicate that **2_{ground}** phase does not contain CH₂Cl₂ molecules (Fig. S6), confirming the release of CH₂Cl₂ upon grinding of **2B**.
15. Thermal treatment of **1G** and **2B** does not show any phase transitions rather decomposes around at 280 °C while only **1G** melt at 280 °C before decomposition (Fig. S7).
16. Concentration-dependent absorption spectroscopy of **2** again observed the monomeric nature at this concentration (Fig. S8).

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