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A gold isocyanide complex with a pendant carboxy group: orthogonal molecular arrangements and hypsochromically shifted luminescent mechanochromism

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The epistatic double hydrogen bonds that arise from the presence of a pendant carboxy group in a gold isocyanide complex result in strong aurophilic interactions in a magenta-emitting polymorph. This is due to the lack of the typically antiparallel dimer arrangements, which often prevent the formation of strong aurophilic interactions. Furthermore, this polymorph shows a hypsochromically shifted luminescent mechanochromism.

Luminescent mechanochromism refers to changes of the emission color of solid or liquid crystalline samples upon mechanical stimulation.[1] Recently, much attention has been focused on the investigation of luminescent mechanochromic compounds on account of potential applications in sensors and recording devices.[2] Luminescent mechanochromic properties are based on changes of the molecular arrangements in response to mechanical stimulation. The key to controlling the properties of such materials is to control their crystal structures via intermolecular interactions, which affects the molecular arrangement patterns in the crystals.

Arylgold(arylisocyanides) are versatile luminescent mechanochromic materials,[3] and we have already reported reversible luminescent mechanochromism,[3a,c] multiple-color mechanochromism,[3c,d] and IR-emissive mechanochromism[3f] for this platform. We have also reported systematic studies on 48 arylgold(arylisocyanide) complexes (**R^1-R^2**; Fig. 1) and their luminescent mechanochromic properties.[3e] These complexes contain various substituents at the two *para*-positions of their benzene rings (R^1 = OMe, Me, H, Cl, CF_3, or CN; R^2 = NMe_2, OMe, Me, H, Cl, CF_3, CN, or NO_2). Out of 48 **R^1-R^2** complexes, we identified 27 single-crystal structures of **R^1-R^2** complexes that exhibit luminescent mechanochromism in their unground phases. The structural analyses revealed that all these complexes form similar antiparallel dimers, which leads to a cancellation of the molecular dipole moments (μ; $\mu \approx 0$ for the dimer; *cf.* white arrows in Fig. 1). Similar to other organic crystals,[2c,4] dipole-dipole interactions should be the predominant intermolecular interactions that determine the crystal structures of mononuclear arylgold(arylisocyanide) complexes, including **R^1-R^2**. However, this circumstance limits further potential alternations of their crystal structures and luminescent properties. For example, the Au···Au distances for **R^1-R^2** in their unground phases, which are a key factor of the luminescence properties of such gold complexes, range from 3.119 Å to 6.044 Å, while their maximum emission wavelength $\lambda_{em,max}$ ranges from 414 nm to 531 nm.[3e]

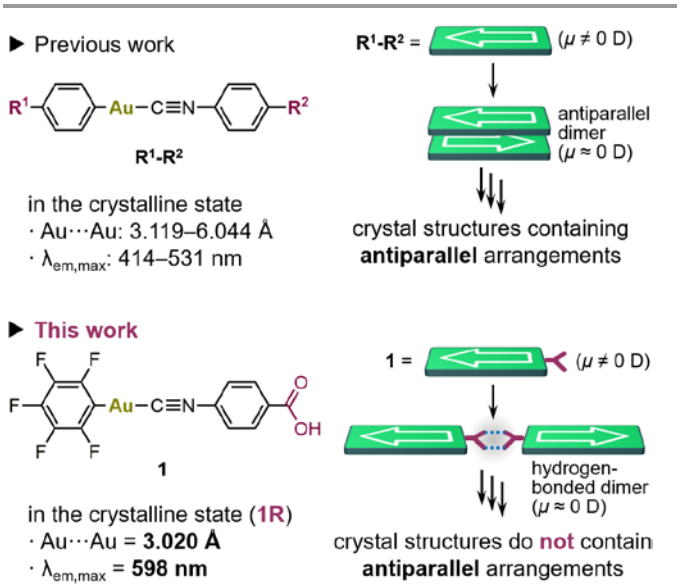


Fig. 1 Chemical structures and schematic illustration of the solid-state molecular arrangements of **R^1-R^2** (**R^1-R^2**: R^1 = OMe, Me, H, Cl, CF_3, or CN; R^2 = NMe_2, OMe, Me, H, Cl, CF_3, CN, or NO_2) and **1**. μ and white arrows indicate dipole moments.

In order to create a new type of crystal-structure motif and mechanochromic properties for the arylgold(arylisocyanide) scaffold, we introduced a functional group that induces strong intermolecular interactions that can dominate other interactions, including dipole-dipole interactions. Monocarboxy-functionalized compounds generally form

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crystal structures that contain double hydrogen bonds at the carboxy moieties,[2a,5] and the resulting hydrogen-bonded dimer is characterized by the absence of an overall dipole moment ($\mu \approx 0$ D). We speculated that monocarboxy-functionalized aryl gold isocyanide complexes could also dimerize via the formation of double hydrogen bonds (Fig. 1) rather than via dipole-dipole interactions, which could lead to a compensation of the molecular dipoles. Consequently, the carboxy-substituted gold isocyanide complexes would form a crystal structure free of antiparallel dimer arrangements. Such molecular packing should promote unique optical properties and phase-transition behavior that cannot be attained for complexes of the type **R^1-R^2**.[3e] Herein, we report gold isocyanide complex **1** (Fig. 1), which contains a carboxy group at the *para*-position of its isocyanide phenyl ligand. We demonstrate that **1** adopts a crystal structure that is based on orthogonally rather than antiparallelly arranged dimers. This study demonstrates that this unique crystal structure facilitates the formation of strong aurophilic interactions that are unattainable in previously reported arylgold(arylisocyanide) complexes, resulting in luminescent mechanochromism and hypsochromically shifted emission wavelengths.

Recrystallization of **1** from dichloromethane/methanol afforded blue- (**1B**) and magenta-emitting crystals (**1R**; Fig. S1). Using THF/hexane as the recrystallization medium, we obtain exclusively **1B**, albeit that we were unable to identify recrystallization conditions that enable the exclusive formation of **1R**. Therefore, we isolated **1R** from the mixed crystal batch by hand. A diluted solution of **1** in THF ($c = 1.0 \times 10^{-5}$ M) shows very weak emission (Fig. S2), suggesting that intermolecular interactions in **1B** and **1R** are important for their emission properties.

Single-crystal XRD measurements on **1B** revealed a typical antiparallel stacking pattern and the presence of two hydrogen bonds at the carboxy moiety (Figs. 2 and S3 as well as Table S1). In **1B**, **1** crystallizes in the triclinic space group *P*-1 and adopts a flat conformation with a dihedral angle ϑ of 4.3(5)° or 5.3(5)° between the C_6F_5 and C_6H_4COOH rings (Fig. 2a). The flat conformation promotes antiparallel stacking with a centroid-to-centroid distance of 3.829(7) Å (Fig. 2b). In these dimers, the nearest Au···Au distance (3.6905(11) Å) is indicative of the absence of aurophilic interactions,[6] as a closer distance between the Au atoms should be restricted by the π-π stacking interactions in the antiparallel dimers (Fig. 2b). All molecules exhibit double hydrogen bonds at their isocyanide carboxy moieties with O···O distances of 2.63(1) Å, which affords hydrogen-bound dimers (Fig. 2c). XRD analyses as well as NMR and TGA measurements indicated that solvent molecules were not included in **1B** (Fig. S5 and S6).

Conversely, single crystals of **1R** are not characterized by antiparallel molecular arrangements and exhibit prominent aurophilic interactions (Figs. 3 and S4 as well as Table S1). In **1R**, **1** crystallizes in the monoclinic space group $P2_1/c$ and adopts a flat conformation (ϑ = 10.9(3)°). Remarkably, an antiparallel stacking arrangement as in **1B** was not observed. In contrast, two molecules of **1** form strong aurophilic interactions (3.0199(8) Å),[6] and arrange orthogonally with a rotational displacement angle of 85.7(6)° (Figs. 3a,b and S4). It should be noted that this intermolecular Au···Au distance is the shortest among the hitherto reported mononuclear gold isocyanide complexes, including all **R^1-R^2** complexes,[3b,e,g] and leads to the formation of an antiparallel arrangement. Similar to **1B**, all molecules of **1** in **1R** also form double hydrogen bonds at their carboxy moieties with an O···O distance of 2.608(9) Å (Fig. 3c).

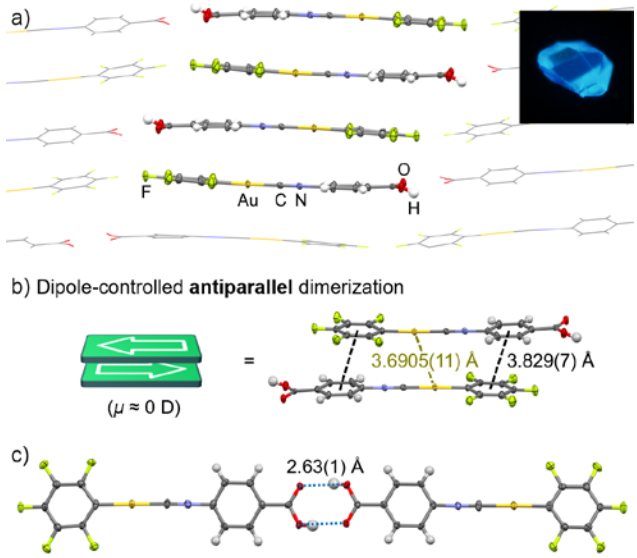


Fig. 2 Single-crystal structure of **1B** with thermal ellipsoids at 50% probability.

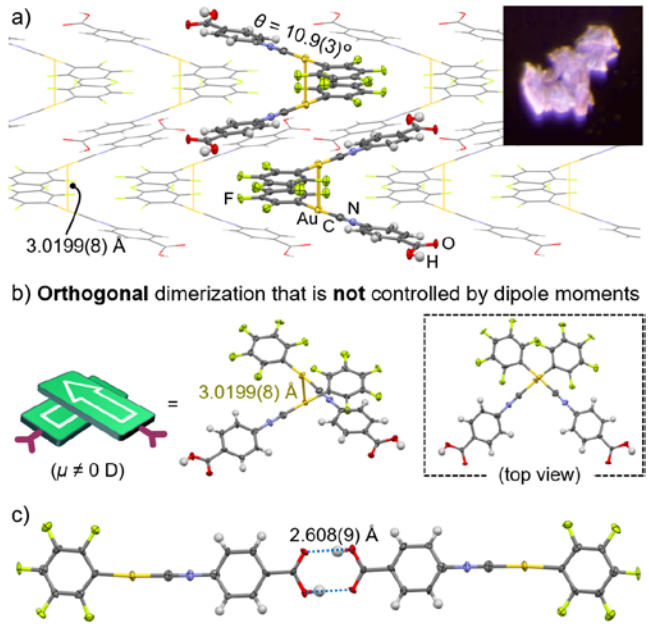


Fig. 3 Single-crystal structure of **1R** with thermal ellipsoids at 50% probability.

The dimerization of **1R** via the formation of double hydrogen bonds should be crucial for the unique orthogonal molecular arrangement observed. In the absence of substituents with strong intermolecular interactions such as the carboxy group, the dimerization of such gold complexes in an antiparallel orientation will initially take place upon

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crystallization from the solution to compensate for the individual molecular dipoles. Consequently, crystal structures based on antiparallel dimers are typically formed as observed for **R^1-R^2**.[3e] However, **1** can dimerize via the formation of double hydrogen bonds, which results in a thermodynamic energy gain and affords a binuclear molecular array (Figs. 2c and 3c). This hydrogen-bonded dimer exhibits an overall dipole moment of $\mu \approx 0$ D, which allows various molecular arrangements including antiparallel stacking (Fig. 2b) and orthogonal molecular arrangements (Fig. 3b). This notion is supported by the crystallization behavior of structurally related binuclear aryl gold isocyanide complexes, which form, in contrast to **R^1-R^2**, antiparallel and orthogonal molecular arrangements.[3c,d]

The emission spectra of **1B** and **1R** were measured under excitation with UV light. **1B** shows a broad emission spectrum with a shoulder at 440 nm and a peak at 474 nm. An absolute emission quantum yield (Φ_{em}) and weighted average emission lifetime (τ_{av}) of 0.19 and 0.71 µs, respectively, were measured (Fig. S7). Conversely, **1R** exhibits an emission spectrum ranging from 400 nm to 700 nm. Two prominent maxima were observed at 474 nm and 598 nm with shoulders at 440 nm and 651 nm. The emission band of **1R** at 400–550 nm, similar to that of **1B**, should be attributed to a contamination with small crystalline particles of **1B**. The $\lambda_{em,max}$ of **1R** (≈ 600 nm) is situated at relatively long wavelengths relative to the 48 **R^1-R^2** complexes, among which the **R^1-R^2** complex with R^1 = OMe and R^2 = CN exhibited the longest $\lambda_{em,max}$ in the crystalline phase (531 nm). Φ_{em} and τ_{av} of **1R** were not measured as we were unable to isolate the amount of pure sample required for such a purpose.

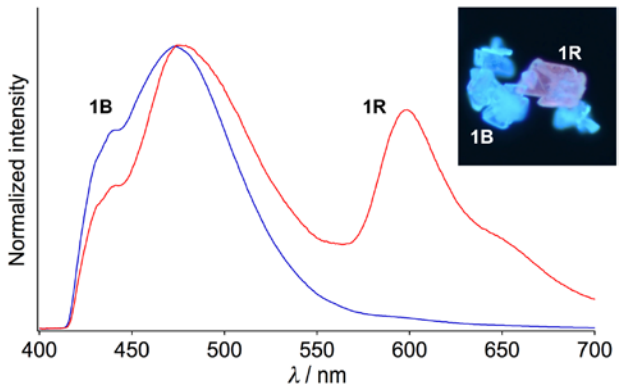


Fig. 4 Emission spectra (λ_{ex} = 365 nm) and photographs (inset; recorded under excitation with UV light) of **1B** and **1R**.

The remarkable magenta emission of **1R** ($\lambda_{em,max} \approx 600$ nm) was attributed to the strong aurophilic interactions in the orthogonal molecular arrangement (Fig. 3). TD-DFT calculations based on the single-crystal structures of **1B** and **1R** indicated a smaller HOMO-LUMO gap for **1R** relative to that of **1B** (Fig. S8), which demonstrates the validity of the calculations. The calculations for **1R** also suggest an antibonding character between the gold atoms and the destabilized HOMO energy level (Fig. S8). These are typical features for strong aurophilic interactions, which contribute to the long-wavelength emission of **1R**. In **1R**, antiparallel dimers are not present and thus, strong aurophilic interactions (Au···Au: 3.0199(8) Å) are formed without compromising the π-π stacking (typically ~3.5 Å) as observed for **1B** (Fig 2b and 3b). This implies that the dimerization through the formation of double hydrogen bonds of the carboxy moiety should be crucial not only for the formation of the orthogonally oriented dimers, but also for the long-wavelength emission. The central role of the carboxy group for the long-wavelength emission of **1R** is also supported by reference complex **2**, which structurally differs from **1** only in as much that the COOH group is replaced with an H atom (Fig. S9). Crystallization of **2** afforded a polymorph that shows only short-wavelength emission ($\lambda_{em,max}$ = 454 nm; Fig. S9) and the formation of typical antiparallel dimers via dipole-dipole interactions was confirmed by single-crystal XRD analyses (Fig. S10 and Table S1).

1B and **1R** show prominent luminescent mechanochromism, albeit that the color change was different. When a crystalline sample of **1B** was mechanically stimulated, its emission color clearly changed from blue to green (Fig. 5a). The resulting powder (**1**$_{ground}$) showed a broad emission spectrum with $\lambda_{em,max}$ = 516 nm (Φ_{em} = 45; τ_{av} = 0.71 µs; Figs. 5b and S7). A powder XRD analysis of **1**$_{ground}$ revealed a featureless trace (Fig. S11). NMR and TGA measurements demonstrated that **1**$_{ground}$ does not contain any solvent molecules (Fig. S5 and S6), which implies that amorphization occurs during the luminescent mechanochromism of **1**.[2c,d,3e,4,6b] IR measurements suggested that the double hydrogen bonds at the carboxy moieties are retained, even in the amorphous phase (Fig. S12). Upon grinding magenta-emitting **1R**, we again obtained a green-emitting powder, whose emission spectrum is essentially similar to that of the ground powder obtained by grinding **1B** (Fig. 5 and S13).[7] This result indicates that the same **1**$_{ground}$ powder was obtained from grinding **1R**.

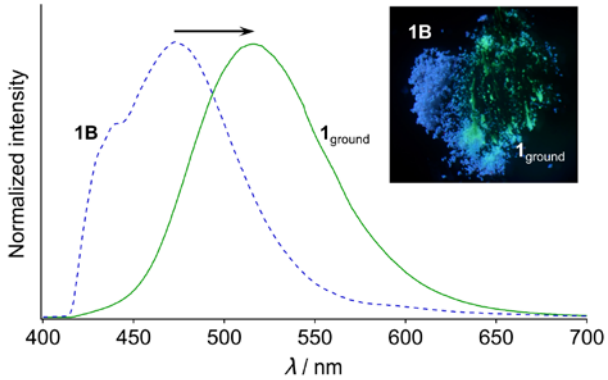


Fig. 5 Emission spectra (λ_{ex} = 365 nm) and photographs (inset; recorded under excitation with UV light) of **1B** and **1**$_{ground}$. The arrow indicates the change upon grinding.

Upon grinding **1B** and **1R**, the alternation of the aurophilic interactions in the solid should occur in opposite fashion, i.e., while they were formed in **1B**, they were weakened in **1R**, resulting in red- and blue-shifted emission bands, respectively

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(Fig. 6). In the amorphous phase of $\mathbf{1}_{ground}$, aurophilic interactions should manifest (Fig. 6, bottom), as typically reported for mechanochromic gold complexes.[3a,c,e,f,8] The formation of aurophilic interactions in $\mathbf{1}_{ground}$ is supported by IR measurements, i.e., the isocyanide stretching vibrations are shifted to lower wavenumbers upon grinding **1B** (Fig. S12), which is indicative of the formation of aurophilic interactions (Fig. 6, blue arrows).[3a,f,9,10] This notion seems feasible when considering the grinding-induced red-shifted emission band of **1B** (Fig. 5). On the other hand, the observed blue-shifted emission color change of **1R** upon grinding indicates that the aurophilic interaction of $\mathbf{1}_{ground}$ is weaker than that in **1R** (Fig. 6, red arrow). This may be explained by the mechano-induced loss of crystallinity of **1R**, concomitant to a loss of the suitable packing for the formation of strong aurophilic interactions through the hydrogen-bond-mediated orthogonal molecular arrangement. It should be noted that hypsochromically shifted emission-color changes have rarely been observed for luminescent mechanochromic compounds.[2c,3g,11]

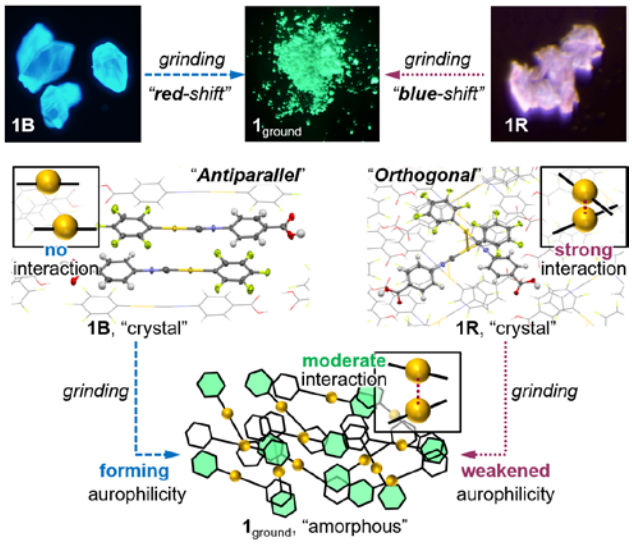


Fig. 6 Photographs (under excitation from UV light at 365 nm) and schematic illustration of the luminescent mechanochromism of **1B** and **1R** based on forming and weakened aurophilic interactions, respectively.

In summary, we have developed a method to control crystal structures of arylgold(arylisocyanides) through the introduction of epistatic intermolecular hydrogen-bond interactions. Single-crystal XRD analyses of magenta-emitting **1R** indicated that strong aurophilic interactions (Au···Au: 3.0199(8) Å) are formed via an orthogonal molecular arrangement. The absence of the typical antiparallel arrangements is caused by the formation of hydrogen-bound dimers that do not exhibit an overall dipole moment. **1R** also showed a hypsochromically shifted luminescent mechanochromism based on a crystal-to-amorphous phase transition and weakened aurophilic interactions *via* the loss of a crystal structure that is favorable for the strong aurophilic interactions. The treatment of **1** with appropriate additives that are expected to interact with the carboxy groups of **1** in order to further express its functionality is currently in progress in our laboratory.

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Conflicts of interest

There are no conflicts of interest to declare.

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10. Although other intermolecular interactions, like π-π stack, can also affect their optical properties, it is unclear if **1**$_{ground}$ forms such intermolecular interactions at the present.
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Correction: A gold isocyanide complex with a pendant carboxy group: orthogonal molecular arrangements and hypsochromically shifted luminescent mechanochromism

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The authors regret that an important reference was omitted from the original article. Espinet et al. had previously reported the synthesis of compound **1** and the single-crystal structure of the polymorph **1R** (CCDC number: 693068). This is listed below as ref. 1 and should have been cited in the original article.
The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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