Electronic Supplementary Information

Mismatched changes of the photoluminescence and crystalline structure of a mechanochromic gold(I) isocyanide complex

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Contents

1. General	S1
2. Optical Properties	S2
3. Single Crystal Structures of 1	S6
4. References	S7

1. General

All commercially available reagents and solvents are of reagent grade and were used without further purification unless otherwise noted. Emission spectra were recorded on a Hitachi F-7000 spectrometer. Fluorescence microscopic spectra were recorded on a Photonic Hamamatsu PMA-12 Multichannel Analyzer. The emission quantum yields of the solid samples were recorded on a Hamamatsu Quantaurus-QY spectrometer with an integrating sphere. Emission lifetime measurements were recorded on a Hamamatsu Quantaurus-Tau spectrometer. Elemental analyses and low- and high resolution mass spectra were recorded at the Center for Instrumental Analysis, Hokkaido University. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 or RICOH CX1 digital cameras. SEM observation was performed with a JSM-6500F SEM (JEOL). Powder diffraction data were recorded at room temperature on a Rigaku SmartLab diffractometer with Cu-K_{α} radiation and a D/teX Ultra detector covering 5–50° (2 θ). Simulated powder patterns were generated with Mercury 3.0 from the single crystal X-ray structures.¹ Synthesis of compound **1** was reported previously.²

2. Optical Properties



Fig. S1 Emission spectra of $1g_{ground}$ (green line) and $1b_{ground}$ (blue line) under excitation at 365 nm.

Table S1 Photophysical properties of various solid phases of 1.

1σ 84 ^d 0970 i 0970 (100) - 866 × 10 ⁵ 1	(5 105
10^{-1} 10^{-1} 10^{-1} 10^{-1} 10^{-1}	$.65 \times 10^{3}$
1b 33^{e} 12.9^{k} $0.970 (0.0427)$ $11.1 (0.263)$ $70.5 (0.695)$ 6.45×10^{3} 1.7	31×10^{4}
$1g_{ground}$ 7.71.130.717 (0.675)1.99 (0.325)- 6.81×10^4 8.	17×10^{5}
1b ground 23 ^d 0.832 ^j 0.358 (0.396) 1.14 (0.604) - 2.76 × 10 ⁵ 9.23 ^d	$.29 \times 10^{5}$

 $a\lambda_{ex} = 315 \text{ nm}. b\lambda_{ex} = 430 \text{ nm}. c\lambda_{ex} = 390 \text{ nm}. d\lambda_{ex} = 370 \text{ nm}. c\lambda_{ex} = 310 \text{ nm}. f\tau_{av} = \sum A_n \tau_n / \sum A_n. g\lambda_{em} = 370 \text{ nm}. b\lambda_{em} = 460 \text{ nm}. i\lambda_{em} = 570 \text{ nm}. j\lambda_{em} = 535 \text{ nm}. k\lambda_{em} = 445 \text{ nm}. lk_r = \Phi / \tau. mk_{nr} = 1 / \tau - k_r.$



Fig. S2 a) Normalized excitation (dashed lines, $\lambda_{em} = 535$ nm) and emission spectra (solid lines, $\lambda_{ex} = 370$ nm) of 1g (green lines) and 1g_{ground} (light green lines). b) Normalized excitation (dashed lines, $\lambda_{em} = 445$ nm for 1b and 535 nm for 1b_{ground}) and emission spectra (solid lines, $\lambda_{ex} = 370$ nm) of 1b (green lines) and 1b_{ground} (light green lines). c) Comparison of excitation (dashed lines) and emission spectra (dashed lines) and emission spectra (blue lines) and emission spectra (blue lines).



Fig. S3. a) Emission decay profiles of 1g (green line, $\lambda_{em} = 535$ nm) and 1g_{ground} (light green line, $\lambda_{em} = 535$ nm). b) Emission decay profiles of 1b (blue line, $\lambda_{em} = 445$ nm) and 1b_{ground} (light green line, $\lambda_{em} = 535$ nm). c) Comparison of emission decay profiles of 1g_{ground} (green line) and 1b_{ground} (blue line).



Fig, S4 Diffuse reflectance spectra of 1g (green line), 1b (blue line), and $1b_{ground}$ (light green line). Both 1b and $1b_{ground}$ have absorption ranging only shorter than 400 nm, while 1g has absorption tale extending up to around 450 nm (denoted as green arrow), which support that the structures of 1b and $1b_{ground}$ in the ground states are different from that of 1g.



Fig. S5 Absorption spectrum of 1g (green line) and emission spectrum of 1b (blue line).

3. Single Crystal Structures of 1



Fig. S6 i) Photographs of the single crystal structure of **1g** taken under UV light. ii) ORTEP representation of hexamer of **1g** connected through multiple intermolecular aurophilic interactions. Phenyl groups except for one carbon atom and dimethylphenyl moieties are omitted for clarity. iii) Packing arrangements of **1g** in which hexameric units are interacted with adjacent ones to form 1-D columnar motives. The data were taken from our previous publication.²



Fig. S7 i) Photographs of the single crystal structure of **1b** taken under UV light. ii) Pentamer derived from the single crystal structures of **1b** 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. c) Packing arrangements of **1b** viewed along the *a* axis. Only hexameric units are represented by space-filling models. The data were taken from our previous publication.²

4. References

- 1. http://www.ccdc.cam.ac.uk/free_services/mercury/downloads/Mercury_3.0/
- 2. T. Seki, K. Sakurada and H. Ito, Angew. Chem. Int. Ed., 2013, 52, 12828–12832.