Electronic Supplementary Information

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

Tomohiro Seki,\* Koh Kobayashi, Takaki Mashimo, Hajime Ito\*

<sup>1</sup>Division of Applied Chemistry & Frontier Chemistry Center (FCC), Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

seki@eng.hokudai.ac.jp hajito@eng.hokudai.ac.jp

Contents		
1. General	<b>S2</b>	
2. Synthesis	<b>S3</b>	
3. Photographs of 1B and 1R under UV light	<b>S4</b>	
4. Optical properties of 1 in THF	<b>S5</b>	
5. Single crystal X-ray analyses	<b>S6</b>	
6. NMR and TGA measurements of 1B and 1ground	<b>S9</b>	
7. Emission decay profiles of 1B and 1ground	<b>S11</b>	
8. TD-DFT calculation of 1B and 1R		
9. Optical properties and crystal structure of 2		
<b>10. Powder diffraction pattern of 1</b> ground		
11. IR absorption and emission spectral change of 1B upon grinding		
12. References	<b>S16</b>	
13. NMR spectra		

#### 1. General

All commercially available reagents and solvents are of reagent grade and were used without further purification unless otherwise noted. Solvents for the synthesis were purchased from commercial suppliers, degassed by three freeze-pump-thaw cycles and further dried over molecular sieves (4 Å). NMR spectra were recorded on a JEOL JNM-ECX400P or JNM-ECS400 spectrometer (<sup>1</sup>H: 400 MHz) using tetramethylsilane as internal standards. Excitation spectra were recorded on a Hitachi F-7000 spectrometer. Emission spectra were measured by using an Olympus fluorescence microscope BX51 equipped with Hamamatsu photonics multichannel analyzer PM-12 and a Hitachi F-7000 spectrometer. Absorption spectra were recorded on a Hitachi U-2910 spectrometer. The emission quantum yields of the solid samples were recorded on a Hamamatsu Quantaurus-QY Plus spectrometer with an integrating sphere. Emission lifetime measurements were recorded on a Hamamatsu Quantaurus-Tau spectrometer. High-resolution mass spectra were recorded at the Global Facility Center at Hokkaido University. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 digital cameras. Powder diffraction data were recorded at on a Rigaku SmartLab diffractometer with Cu-K<sub>α</sub> radiation and D/teX Ultra detector covering 5–60° ( $2\theta$ ).

*X-ray diffraction analyses*: Single crystal X-ray structural analyses were carried out on a Rigaku R-AXIS RAPID diffractometer or Rigaku XtaLAB PRO MM007 diffractometer using graphite monochromated Mo-K<sub> $\alpha$ </sub> radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure or Olex crystallographic software package except for refinement, which was performed using SHELXL.<sup>1</sup> Simulated powder patterns were generated with Mercury 3.7<sup>2</sup> from the structures determined by single crystal diffraction analyses.

**DFT calculation**: All calculations were performed using the Gaussian 09W (revision C.01 and E.01) and Gaussian 09 (revision C.01 and E.01) program package.<sup>3</sup> The singlet state TD-DFT calculations of the tetramer of **1B** and **1R** were performed. In the calculations, the B3LYP functional and the SDD basis set were used. The geometries of the tetramers were taken from the single-crystal structures of **1B** and **1R**. The positions of heavy atoms were fixed and only the positions of H atoms were optimized using the Gaussian 09 (B3LYP/SDD) prior to the TD-DFT measurements.

#### 2. Synthesis

Synthesis of gold(I) isocyanide complex 1



A mixture of pentafluorophenyl(tetrahydrothiophen)gold(I) (452.2 mg, 1.0 mmol) and 4carboxylisocyanidebenzene (176.6 mg, 1.2 mmol)<sup>4</sup> was stirred in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) for 5 h under a nitrogen atmosphere at room temperature. The emerging precipitate was collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub>, and dried in vacuo to obtain complex **1** as white solid (305.3 mg, 0.597 mmol, 60%). <sup>1</sup>H NMR (392 MHz, THF-*d*<sub>8</sub>,  $\delta$ ): 6.12–6.22 (m, 2H), 6.42–6.54 (m, 2H). OH proton signal can not be observed likely due to facile exchange with a proton of residual H<sub>2</sub>O in CDCl<sub>3</sub>. The poor solubility of **1** in common organic solvents hampered <sup>13</sup>C NMR measurements. HRMS-EI (*m/z*): [M<sup>+</sup>] calcd for C<sub>14</sub>H<sub>5</sub>AuF<sub>5</sub>NO<sub>2</sub> 510.99060; found, 510.99060.

## 3. Photographs of 1B and 1R under UV light



**Fig. S1** Photograph of **1B** and **1R** formed concomitantly by a recrystallization which is taken under the excitation at 365 nm.

## 4. Optical properties of 1 in THF



**Fig. S2** UV/vis absorption (black line), excitation ( $\lambda_{em} = 413$  nm, purple line), and emission spectra ( $\lambda_{ex} = 276$  nm, blue line) of **1** in THF at room temperature. [**1**] =  $1.0 \times 10^{-5}$  M.

# 5. Single crystal X-ray analyses

Polymorph	1B	1R	2
CCDC number	1858874	1858875	1858876
Empirical Formula	C <sub>14</sub> H <sub>5</sub> AuF <sub>5</sub> NO <sub>2</sub>	C <sub>14</sub> H <sub>5</sub> AuF <sub>5</sub> NO <sub>2</sub>	C <sub>13</sub> H <sub>5</sub> AuF <sub>5</sub> N
Formula Weight	511.16	511.16	467.15
Crystal System	triclinic	monoclinic	triclinic
Crystal Size / mm	$0.521\times0.152\times0.102$	$0.101\times 0.069\times 0.024$	$0.34 \times 0.10 \times 0.07$
<i>a</i> / Å	7.3857(3)	13.4101(9)	7.2397(2)
b/Å	7.4524(3)	7.7601(5)	7.3439(2)
<i>c</i> / Å	27.7545(9)	13.0837(12)	12.3992(3)
α / °	82.335(3)	90	77.440(2)
$\beta$ / °	89.173(3)	97.493(7)	75.353(2)
γ / °	60.856(4)	90	71.305(3)
$V/\text{\AA}^3$	1320.06(10)	1349.91(18)	597.43(3)
Space Group	<i>P</i> -1	<i>P</i> 2/ <i>c</i>	<i>P</i> -1
Z value	4	4	2
$D_{ m calc}$ / g·cm <sup>-3</sup>	2.572	2.515	2.597
Temperature / K	123	123	123
No. of Reflections	Total: 11383	Total: 6129	Total: 7833
Measured	Unique: N/A <sup>a</sup>	Unique: 2423	Unique: 2686
	$(R_{\text{int}}: N/A^{a})$	$(R_{\rm int} = 0.0871)$	$(R_{\rm int} = 0.0261)$
Residuals: R <sub>1</sub>	7.81	6.63	1.78
$(I > 2.00\sigma(I)) / \%$			
Residuals: wR <sub>2</sub>	23.88	17.04	4.38
(All reflections) / %			
Goodness of Fit	1.106	1.101	1.057
(GOF)			
Maximum peak in	5.05 e-	3.46 e <sup>-</sup>	1.31 e-
Final Diff. Map / $Å^3$			
Minimum peak in	-3.36 e-	-2.81 e <sup>-</sup>	-1.35 e-
Final Diff. Map / Å <sup>3</sup>			

Table S1. X-ray crystallographic data for 1B, 1R, and 2.

<sup>a</sup>: Not available because of the twin analyses.



Fig. S3 Single-crystal structure and photograph (under excitation at 365 nm) of 1B.



Fig. S4 Single-crystal structure and photograph (under excitation at 365 nm) of 1R.

#### 6. NMR and TGA measurements of 1B and 1ground



Fig. S5 NMR spectra of 1B (top) and 1<sub>ground</sub> (bottom) in THF-d<sub>8</sub>.



Fig. S6 TGA profiles of 1B (top) and  $1_{ground}$  (bottom) with the heating rate of 5 °C/min.

#### 7. Emission decay profiles of 1B and 1ground



**Fig. S7** Emission decay profiles of **1B** and  $1_{\text{ground}}$ .  $\lambda_{\text{ex}} = 365 \text{ nm}$ .  $\lambda_{\text{em}} = 474 \text{ nm}$  (**1B**), 516 nm ( $1_{\text{ground}}$ ). The curve fitting results are summarized as follows:

**1B**:  $\tau_1 = 0.40 \ \mu s \ (A_1 = 0.59); \ \tau_2 = 0.91 \ \mu s \ (A_2 = 0.41); \ \tau_{av} = 0.71 \ \mu s.$ 

**1**<sub>ground</sub>:  $\tau = 0.71 \ \mu s$ .

Here,  $\tau_{av}$  is defined as  $(\Sigma A_i \tau_i^2)/(\Sigma A_i \tau_i)$ .

### 8. TD-DFT calculation of 1B and 1R



Fig. S8 Structures and frontier molecular orbitals of the tetramers derived from the single crystals of 1B and 1R. The frontier molecular orbitals are based on the results of the DFT calculation (B3LYP/SDD).

### 9. Optical properties and crystal structure of 2



Fig. S9 Structure and emission spectrum ( $\lambda_{ex} = 365 \text{ nm}$ ) of 2. Inset shows a photograph of 2 taken under 365 nm.



Fig. S10 Single-crystal structures of 2.

# **<u>10. Powder diffraction pattern of 1ground</u>**



Fig. S11 Simulated powder patterns of 1B and 1R derived from the corresponding single-crystal structures and powder X-ray diffraction pattern of  $1_{ground}$ .

#### 11. IR absorption and emission spectral change of 1B upon grinding



Fig. S12 IR spectra (left) and the magnified spectral region (right) of 1B (blue lines) and 1<sub>ground</sub> (green lines).

Note 1: Broad absorption of O-H stretching vibration should indicate the formation hydrogen bonds. Note 2: As we intensely investigated previously,<sup>5</sup> the slight spectral shift of the absorption of the  $C \equiv N$  stretching mode of the gold complexes to lower wavenumbers is indicative of the formation of the aurophilic interactions.



Fig. S13 Emission spectra of 1R and  $1_{ground}$  (obtained by grinding 1B and 1R) excited at 365 nm. The arrow shows the change upon mechanical stimulation. The spectral shift of 1R upon grinding would not be completed because of the only small amount of 1R have to be used as an unground sample for this experiment due to the difficulty of the preparation.

#### **12. References**

- 1. G. M. Sheldrick Acta Crystallogr., Sect. A 2008, 64, 112.
- 2. http://www.ccdc.cam.ac.uk/free\_services/mercury/downloads/Mercury\_3.0/
- Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 4. S. Coco, E. Espinet, P. Espinet and I. Palape, *Dalton Trans.* 2007, 3267.
- 5. T. Seki, N. Tokodai, S. Omagari, T. Nakanishi, Y. Hasegawa, T. Iwasa, T. Taketsugu, H. Ito, *J. Am. Chem. Soc.* **2017**, *139*, 6514.