Electronic Supplementary Information

# Low-Temperature-Selective Luminescent Mechanochromism of a Thienyl Gold Isocyanide Complex

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### 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; <sup>13</sup>C: 99.5 MHz) using tetramethylsilane and CDCl<sub>3</sub> as internal standards, respectively. 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. 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. DSC measurements were recorded on a SII DSC 7020 heat flux meter. Elemental analyses and low- and 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 or RICOH CX1 digital cameras. Powder diffraction data were recorded at on a Rigaku SmartLab diffractometer with Cu-K<sub>a</sub> radiation and D/teX Ultra detector covering 5-60° (2 $\theta$ ). A cooling/heating stage on JHC 10002L was used for temperature changes of solid samples.

*X-ray diffraction analyses*: Single crystal X-ray structural analyses were carried out on a Rigaku R-AXIS RAPID 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 crystallographic software package except for refinement, which was performed using SHELXL-2014.<sup>1</sup> Simulated powder patterns were generated with Mercury 3.7<sup>2</sup> from the structures determined by single crystal diffraction analyses.

#### 2. Synthesis



To a solution of 2-bromothiophene (336 mg, 2.25 mmol) in 5 ml diethylether at -78 °C under nitrogen atmosphere, a solution of *n*-BuLi in THF (1.4 ml, 2.25 mmol, 1.63 M) was added dropwise with stirring. The reaction was allowed to warm to room temperature and was stirred for 1 hour to give a solution of 2.25 mmol of 2-thienyl lithium. After cooling the resulting solution to -78 °C, a solid sample of chloro(phenyl isocyanide)gold(I) (503 mg, 1.5 mmol) was added with stirring. The reaction was allowed to warm to 0 °C. After 2 h stirring, the reaction was quenched by the addition of a phosphate buffer solution and then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times and washed with H<sub>2</sub>O and brine. The organic layers were collected and dried over MgSO<sub>4</sub>. After filtration, the solvent was removed in vacuo. Further purification by short column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:1) gave a white solid of **1** (375 mg, 0.98 mmol, 65 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.13 (d, *J* = 3.2 Hz, 1H), 7.38 (dd, *J* = 3.2 Hz, 5.2 Hz, 1H), 7.50–7.61 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 124.8 (*C*), 126.7 (*C*H), 126.9 (*C*H), 127.6 (*C*H), 129.9 (*C*H), 131.3 (*C*H), 134.4 (*C*H), 158.4 (*C*), 159.5 (*C*). MS-EI (*m*/*z*): [M+Na]<sup>+</sup> calcd for C<sub>11</sub>H<sub>8</sub>AuNS, 405.99407; found, 405.99407. Anal. Calcd for C<sub>11</sub>H<sub>8</sub>AuNS: C, 34.48; H, 2.10; N, 3.66; found: C, 34.19; H, 1.94; N, 3.51.

# 3. Optical properties of 1 in solution



**Fig. S1** UV/vis absorption (black line), excitation ( $\lambda_{em} = 450$  nm, orange line) and emission spectra ( $\lambda_{ex} = 280$  nm, red line) of **1** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. [**1**] =  $3.2 \times 10^{-6}$  M.

## 4. DSC analysis of 1R upon heating



Fig. S2 DSC profile of 1R at a heating rate of 5 °C min<sup>-1</sup>. The peak at 110 °C is assignable to decomposition which was visually confirmed. Below decomposition temperature at 110 °C, no peak was observed in DSC analyses.

### 5. Optical properties of powder of 1R and 1R<sub>Blue</sub>



**Fig. S3** a) Photographs of **1R** taken at 25 °C and **1R**<sub>Blue</sub> taken at -75 °C with the excitation at 365 nm. b) Emission spectral changes upon cooling **1R** from 25 °C (red line) to -150 °C (blue line) with the excitation at 365 nm. Measurement temperature: 25, 0, -25, -50, -75, -100, -150 °C.



Fig. S4 Excitation spectra of 1R (25 °C, red lines) and  $1R_{Blue}$  (-150 °C, blue lines) monitored at a) 458 nm and b) 645 nm.



**Fig. S5** a) Photographs of a heating/cooling stage and b) Photographs of the heating/cooling stage within plastic bag filled with nitrogen gas. c) Photographs of a microscope in nitrogen-filled plastic bag.

Note: To prevent the formation of ice on 1, we prepared for a plastic bag filled with nitrogen gas into which 1R, a heating/cooling stage, and a spatula were placed, then mechanical stimulation is applied to afford 1G. Under air, mechanochromism of 1 at low temperature is also observed.



### 6. Recovery of the 1R from 1G upon warming

**Fig. S6** a) Photographs of solid samples of **1R** (25 °C, left) and **1G** (-75 °C, middle) and a solid obtained after warming **1G** (denoted **1R''**, 25 °C, right) with the excitation at 365 nm. b) Emission spectra of solid samples of **1R** (25 °C, black dotted line) and **1G** (-75 °C, green line) and a solid obtained after warming **1G** (**1R''**, 25 °C, red solid line).

# 7. Optical properties and crystal structures of the single crystals of 1



**Fig. S7** Emission spectra of a powder sample of **1R** (solid line) and red-emitting single crystal obtained by recrystallization (dotted line) with the excitation at 365 nm. Inset shows photographs of a red-emitting single crystal obtained by recrystallization (upper) and a powder sample of **1R** (lower) taken under UV illumination.









Fig. S8 Photographs and single-crystal structures of a) red-emitting crystal of 1 (measured at 25 °C) and b) blue-emitting crystal of 1 (measured at -150 °), which are corresponding to 1R and 1R<sub>Blue</sub>, respectively.

Polymorph	1R	1R <sub>Blue</sub>
CCDC Name	1537737	1537738
Empirical Formula	C <sub>11</sub> H <sub>8</sub> AuNS	C <sub>11</sub> H <sub>8</sub> AuNS
Formula Weight	383.22	383.22
Crystal System	triclinic	triclinic
Crystal Size / mm	$0.114 \times 0.068 \times 0.015$	$0.114\times 0.068\times 0.015$
<i>a</i> / Å	5.850(3)	5.7510(11)
<i>b</i> / Å	8.472(4)	8.2449(13)
<i>c</i> / Å	11.703(6)	11.8285(19)
α / °	102.488(10)	103.379(4)
β/°	99.645(9)	99.477(5)
y / °	96.731(9)	95.776(5)
$V / \text{\AA}^3$	551.1(5)	532.54(15)
Space Group	<i>P</i> -1 (#2)	P-1 (#2)
Z value	2	2
$D_{\text{calc}} / \text{g} \cdot \text{cm}^{-3}$	2.309	2.390
Temperature / K	298	123
$2\theta_{ m max}$ / °	55.0	55.0
$\mu \left( \mathrm{MoK}_{\mathrm{\alpha}} \right) / \mathrm{cm}^{-1}$	135.397	140.128
No. of Reflections	Total: 5278	Total: 5261
Measured	Unique : 2496	Unique : 2423
	$(R_{\rm int} = 0.1115)$	$(R_{\rm int} = 0.0943)$
Residuals: $R_1$	7.25	7.76.
$(I > 2.00\sigma (I)) / \%$		
Residuals: $wR_2$	17.52	13.94
(All reflections) / %		
Goodness of Fit (GOF)	0.978	1.136
Maximum peak in	0.77 e-	2.53 e <sup>-</sup>
Final Diff. Map / Å <sup>3</sup>		
Minimum peak in	_1.15. e⁻	-5.17 e <sup>-</sup>
Final Diff. Map / Å <sup>3</sup>		

Table S1. Summary of X-ray crystallographic data for 1 at -150 °C and 25 °C.



Fig. S9 a) Photographs of a crystal of 1 under UV light at various temperature. b) Emission spectral changes of single crystals of 1 at range from 25 °C to -150 °C.



Fig. S10 Emission spectra of a powder sample of  $1R_{Blue}$  (-75 °C, solid line) and blue-emitting single crystal (-75 °C, dotted line) with the excitation at 365 nm. Inset shows photographs of a blue-emitting single crystal obtained by recrystallization (-75 °C, upper) and a powder sample of  $1R_{Blue}$  (-75 °C, lower) taken under UV illumination.



Fig. S11 Simulated powder XRD patterns derived from the red- and blue-emitting single crystals, corresponding to 1R and  $1R_{Blue}$ , respectively.

### 8. DSC analysis of 1R within the low temperature

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**Fig. S12** DSC analysis of **1** ranging from  $-120 \,^{\circ}$ C to 20  $^{\circ}$ C at a heating rate of 5  $^{\circ}$ C min<sup>-1</sup>. Because of limitation of our instrument, we can not perform DSC analyses of samples during cooling. Thus, this measurement is performed upon heating of **1R**<sub>Blue</sub> from  $-120 \,^{\circ}$ C.

# 9. Powder XRD analyses



**Fig. S13** Powder XRD pattern of **1R** at room temperature (upper pattern) and simulated powder XRD pattern of the red-emitting single crystal of **1** (lower pattern).



Fig. S14 a) Temperature-dependent powder XRD patterns of 1. Measurement temperature: 25, 0, -25, -50, -75, -100, -150 °C. b–e) Plots of a position of specific peaks with respect to temperature, indicating gradual peak shifts.



Fig. S15 Powder XRD pattern of  $1R_{Blue}$  at -150 °C (upper pattern) and simulated powder XRD pattern of the blue-emitting single crystal of 1 (lower pattern).



Fig. S16 Photographs when 1G samples for powder XRD analyses were prepared.

Note: For the powder XRD measurements of 1G, the ground powder sample was prepared under a nitrogen atmosphere as follows: into a plastic bag filled with nitrogen gas, a test tube was inserted that contained 1R and a stirring bar (Fig. S16a). This test tube was inserted in a liquid nitrogen bath  $(1R \rightarrow 1R_{Blue})$ , before stirring was applied for 3 h  $(1R_{Blue}\rightarrow 1G)$ . The sample stage of the powder XRD apparatus was also covered with a nitrogen-filled plastic bag and cooled to -150 °C (Fig. S16b). Then, the 1G sample in the test tube was transferred to the cooled sample stage in order to carry out the powder XRD measurements (Fig. S16c). After confirming the green photoluminescence of the sample (Fig. S16d), the sample stage chamber was sealed and evacuated, before the powder XRD measurement was carried out.

### **10. Photophysical properties of 1**



Fig. S17 Emission decay profiles of 1R,  $1R_{Blue}$ , and 1G with the excitation at 370 nm. Monitored emission wavelengths are 464 nm for 1R and  $1R_{Blue}$ , 519 nm for 1G, and 640 nm for 1R and  $1R_{Blue}$ .

	χ/-	$ au_{\mathrm{av}}^{\mathrm{b,c}}$ / $\mu\mathrm{s}$	τ <sub>1</sub> / μs (A / -)	τ <sub>2</sub> / μs (A / -)	τ <sub>3</sub> / μs (A / -)
<b>1R</b> (at 640 nm) <sup>a</sup>	1.11	83	1.4 (0.75)	27.2 (0.10)	99.1 (0.15)
<b>1R</b> (at 464 nm) <sup>a</sup>	1.38	1	0.50 (0.61)	1.73 (0.39)	_
$1\mathbf{R}_{\text{Blue}}$ (at 640 nm) <sup>a</sup>	1.30	127	0.52 (0.62)	65.3 (0.30)	203.5 (0.08)
$\frac{1R_{Blue}}{(at 464 nm)^{a}}$	1.26	41	0.43 (0.77)	31.0 (0.16)	54.9 (0.08)
1 <b>G</b> (at 519 nm) <sup>a</sup>	_ <sup>d</sup>	_d	_ <sup>d</sup>	_d	_d

Table S2. Summary of photophysical data of 1.

<sup>a</sup>: Monitored emission wavelength is shown in parentheses. <sup>b</sup>:  $\tau_{av}$  is defined as:  $\Sigma(A_n\tau_n^2) / \Sigma(A_n\tau_n)$ . <sup>c</sup>:  $\lambda_{ex} = 370$  nm. <sup>d</sup>: Fitting failed.



Fig. S18 Photographs of solid samples of 1 taken under UV light when mechanically stimulated at various temperature. It should be note that we also confirmed that 1G is intact for more than one day at -78 °C, when 1G was obtained by mechanical stimulation with a stirring bar in a test tube, where the sample can be kept easily at -78 °C for longer periods by using a dry ice/hexane bath.

This experiment was carried out as follows: the heating/cooling stage containing **1R** on a glass plate was sealed with a lid, not with plastic bag (see Figure A below), in order to prevent the sample from being exposed to too much air. The sample was cooled to 0, -25, or -75 °C, before the seal was opened to scratch the sample ten times with a spatula (Figure B). Subsequently, an emission-color change of the sample to green was observed at the scratched areas (Fig. S18). After ten scratches, the lid was closed again (Figure C) and we examined the time necessary for the reverse emission-color changes.



#### 11. NMR spectra



Fig. S19 <sup>1</sup>H NMR spectrum of 1 dissolved in CDCl<sub>3</sub>.



Fig. S20<sup>13</sup>C NMR spectrum of 1 dissolved in CDCl<sub>3</sub>.

### 12. References

- 1. Sheldrick, G. M. Acta Crystallogr. Sect. A 2015, 71, 3.
- 2. http://www.ccdc.cam.ac.uk/free\_services/mercury/downloads/Mercury\_3.0/