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Author(s)	Seki, Tomohiro; Kobayashi, Koh; Ito, Hajime
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Low-Temperature-Selective Luminescent Mechanochromism of a Thienyl Gold Isocyanide Complex

Tomohiro Seki,* Koh Kobayashi, and Hajime Ito*

¹Division 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

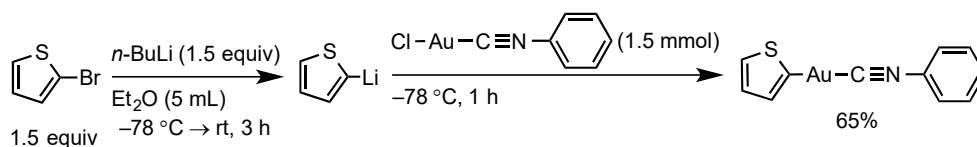
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1. General

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 (^1H : 400 MHz; ^{13}C : 99.5 MHz) using tetramethylsilane and CDCl_3 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 Quantaaurus-QY Plus spectrometer with an integrating sphere. Emission lifetime measurements were recorded on a Hamamatsu Quantaaurus-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_α radiation and D/teX Ultra detector covering $5\text{--}60^\circ$ (2θ). 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_α 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-2014.¹ Simulated powder patterns were generated with Mercury 3.7² 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 $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere, a solution of $n\text{-BuLi}$ 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-thienyllithium. After cooling the resulting solution to $-78\text{ }^\circ\text{C}$, 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 $0\text{ }^\circ\text{C}$. After 2 h stirring, the reaction was quenched by the addition of a phosphate buffer solution and then extracted with CH_2Cl_2 three times and washed with H_2O and brine. The organic layers were collected and dried over MgSO_4 . After filtration, the solvent was removed in vacuo. Further purification by short column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:1$) gave a white solid of **1** (375 mg, 0.98 mmol, 65 %). ^1H NMR (400 MHz, CDCl_3 , δ): 7.13 (d, $J = 3.2\text{ Hz}$, 1H), 7.38 (dd, $J = 3.2\text{ Hz}$, 5.2 Hz, 1H), 7.50–7.61 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 124.8 (C), 126.7 (CH), 126.9 (CH), 127.6 (CH), 129.9 (CH), 131.3 (CH), 134.4 (CH), 158.4 (C), 159.5 (C). MS-EI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_8\text{AuNS}$, 405.99407; found, 405.99407. Anal. Calcd for $\text{C}_{11}\text{H}_8\text{AuNS}$: 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

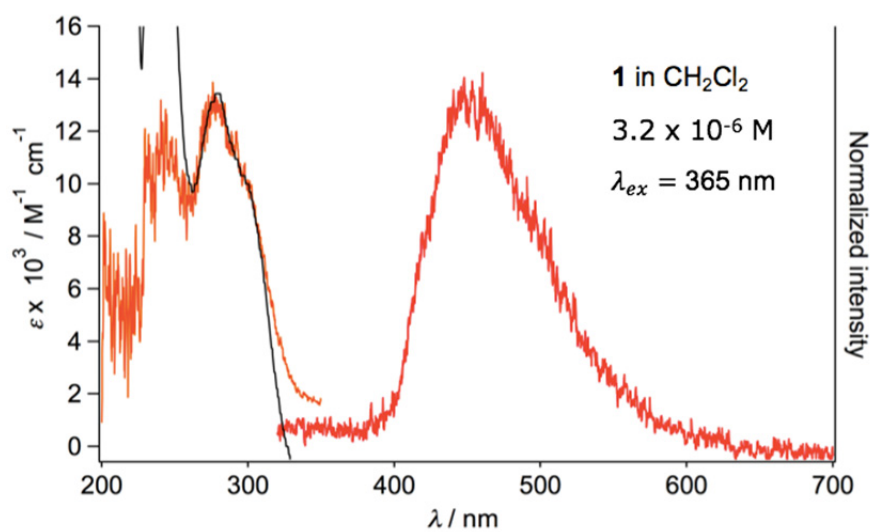


Fig. S1 UV/vis absorption (black line), excitation ($\lambda_{em} = 450 \text{ nm}$, orange line) and emission spectra ($\lambda_{ex} = 280 \text{ nm}$, red line) of **1** in CH_2Cl_2 at room temperature. $[\mathbf{1}] = 3.2 \times 10^{-6} \text{ M}$.

4. DSC analysis of 1R upon heating

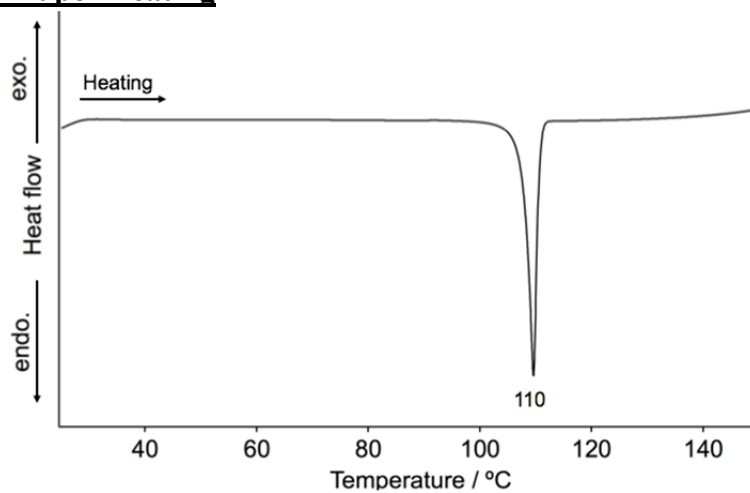


Fig. S2 DSC profile of **1R** at a heating rate of 5 °C min⁻¹. The peak at 110 °C is assignable to decomposition which was visually confirmed. Below decomposition temperature at 110 °C, no peak was observed in DSC analyses.

5. Optical properties of powder of **1R** and **1R_{Blue}**

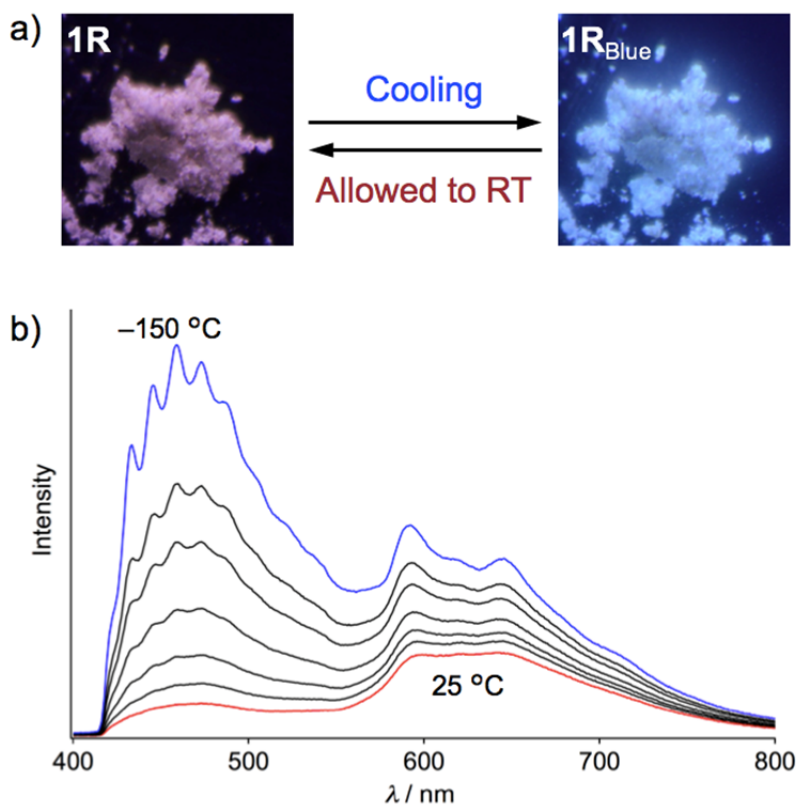


Fig. S3 a) Photographs of **1R** taken at 25 °C and **1R_{Blue}** taken at -75 °C with the excitation at 365 nm. b) Emission spectral changes upon cooling **1R** from 25 °C (red line) to -150 °C (blue line) with the excitation at 365 nm. Measurement temperature: 25, 0, -25, -50, -75, -100, -150 °C.

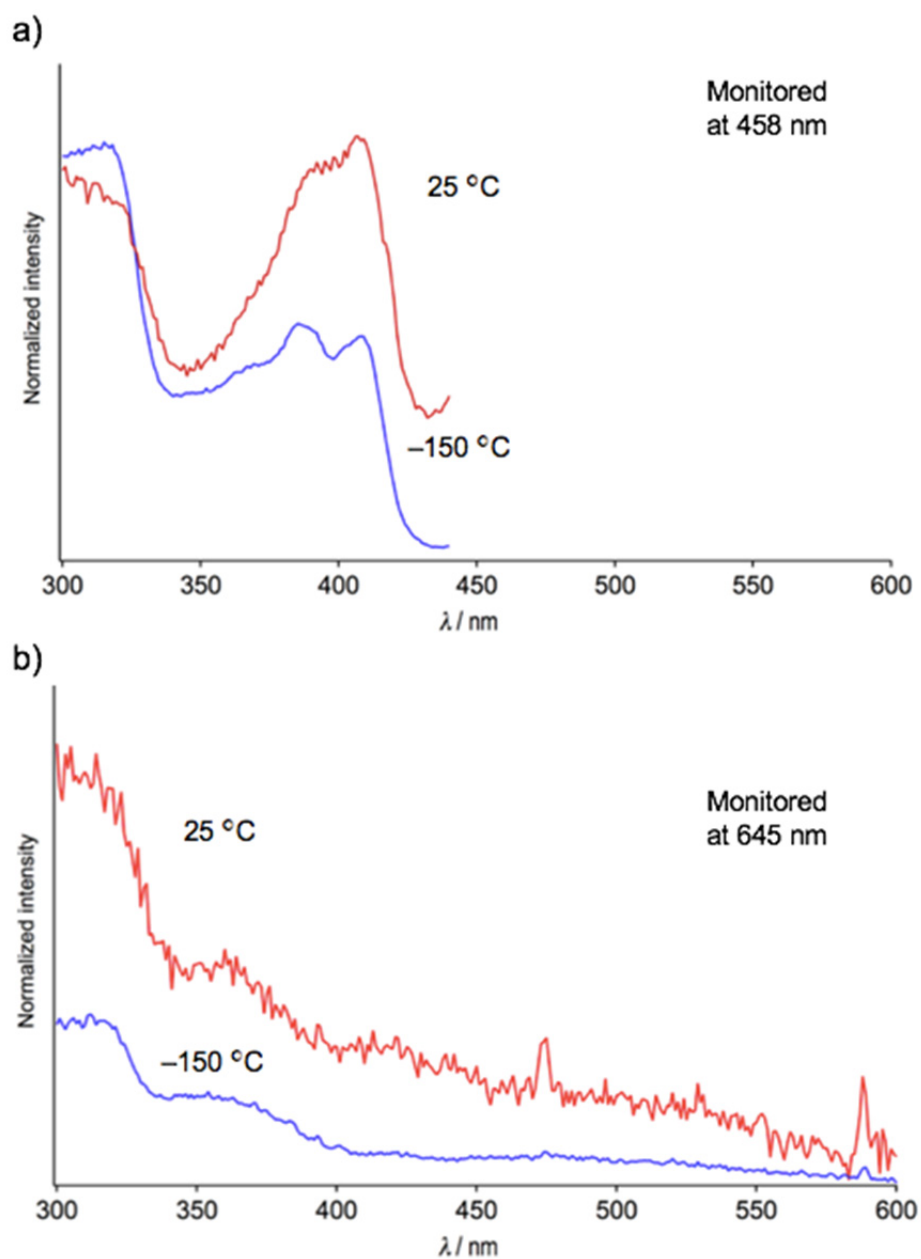


Fig. S4 Excitation spectra of **1R** (25 °C, red lines) and **1R_{Blue}** (-150 °C, blue lines) monitored at a) 458 nm and b) 645 nm.

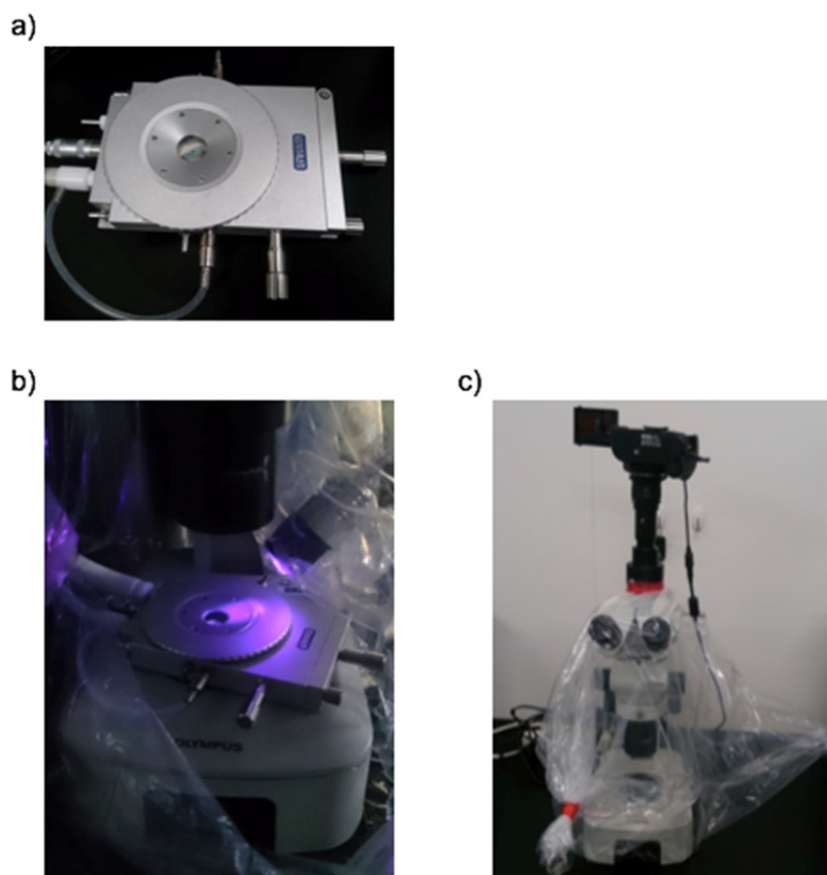


Fig. S5 a) Photographs of a heating/cooling stage and b) Photographs of the heating/cooling stage within plastic bag filled with nitrogen gas. c) Photographs of a microscope in nitrogen-filled plastic bag.

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

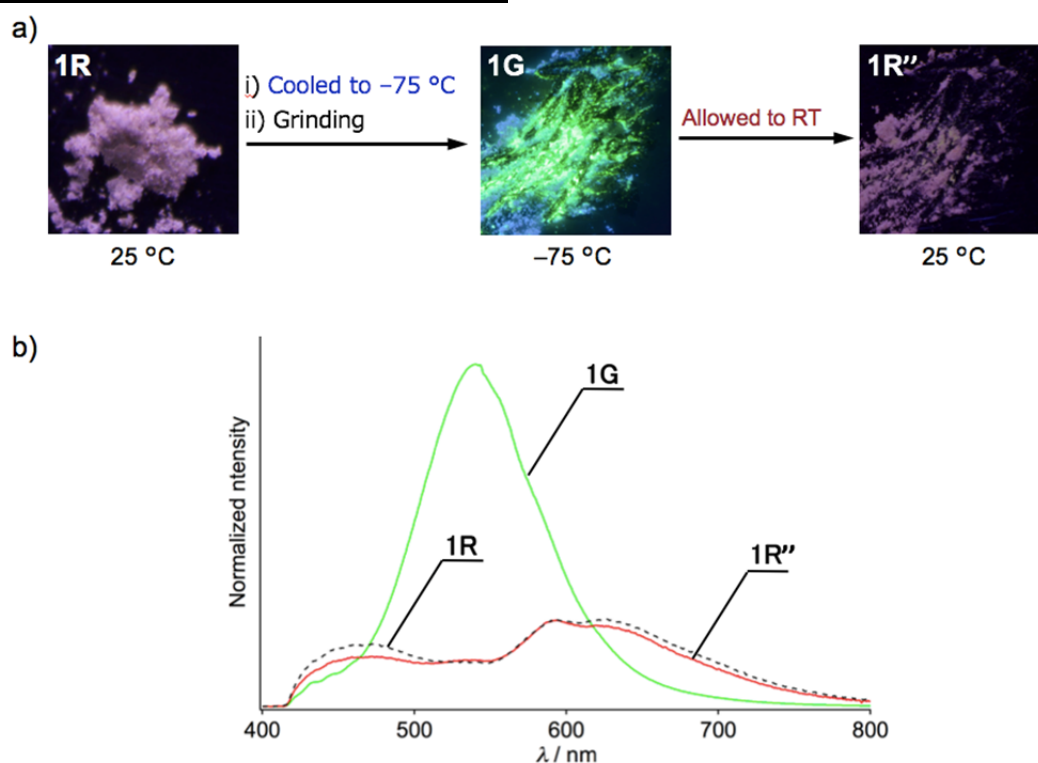


Fig. S6 a) Photographs of solid samples of **1R** (25 °C, left) and **1G** (-75 °C, middle) and a solid obtained after warming **1G** (denoted **1R''**, 25 °C, right) with the excitation at 365 nm. b) Emission spectra of solid samples of **1R** (25 °C, black dotted line) and **1G** (-75 °C, green line)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

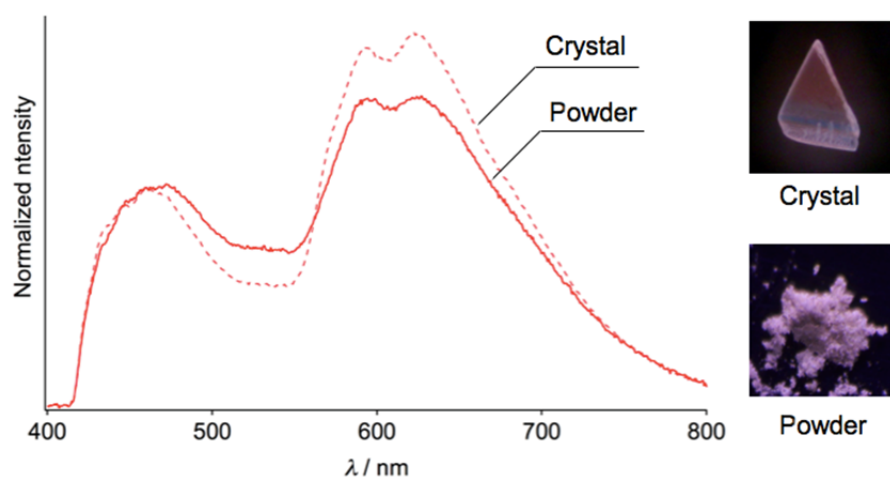
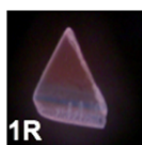
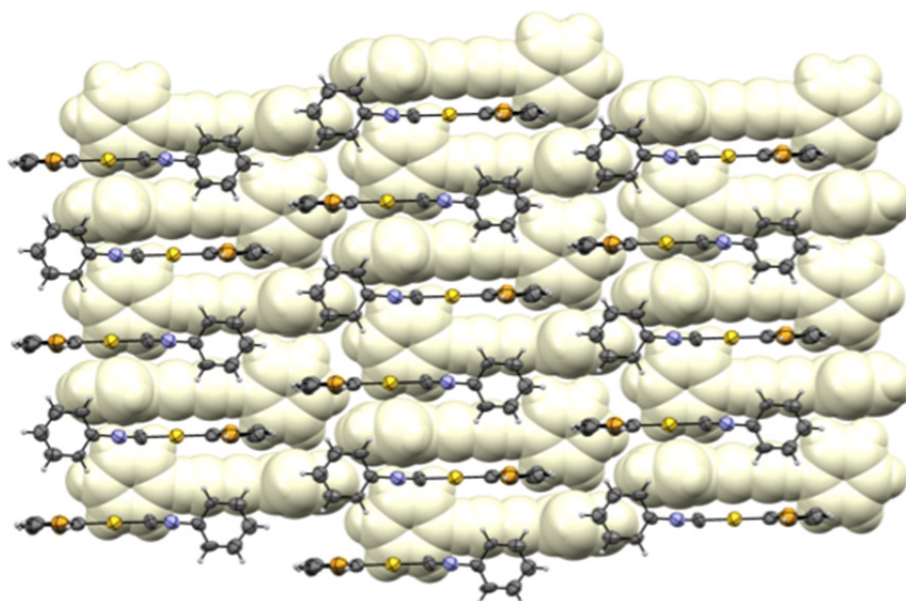
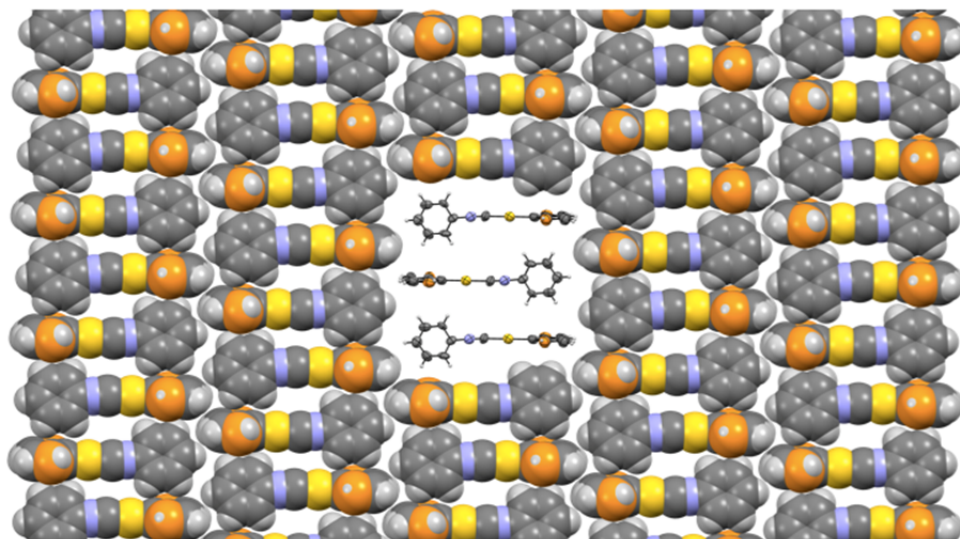
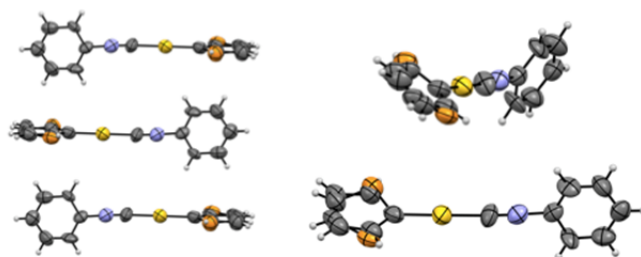


Fig. S7 Emission spectra of a powder sample of **1R** (solid line) and red-emitting single crystal obtained by recrystallization (dotted line) with the excitation at 365 nm. Inset shows photographs of a red-emitting single crystal obtained by recrystallization (upper) and a powder sample of **1R** (lower)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

a)



25 °C



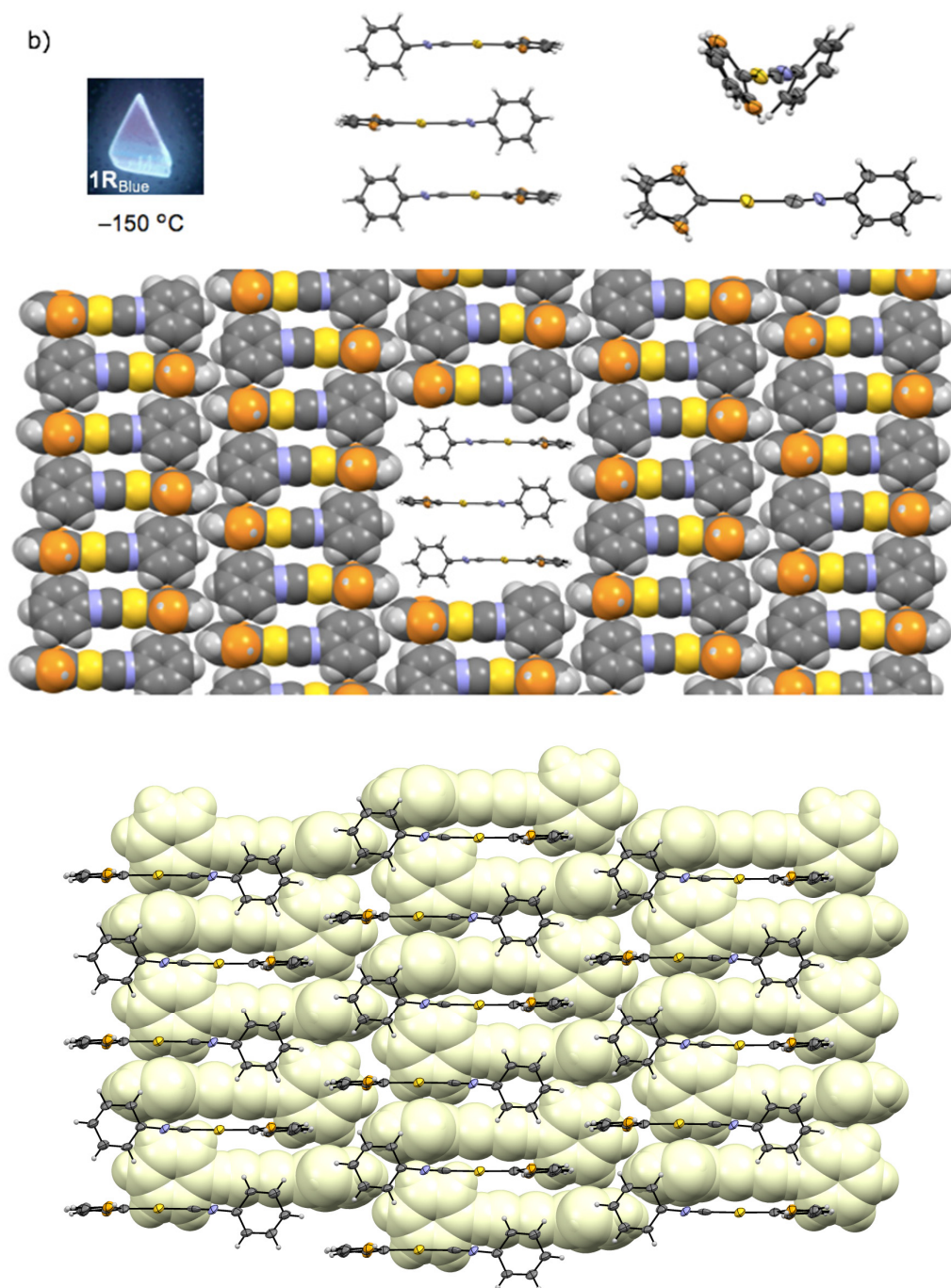


Fig. S8 Photographs and single-crystal structures of a) red-emitting crystal of **1** (measured at 25 °C) and b) blue-emitting crystal of **1** (measured at -150 °), which are corresponding to **1R** and **1R_{Blue}**, respectively.

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

Polymorph	1R	1R_{Blue}
CCDC Name	1537737	1537738
Empirical Formula	C ₁₁ H ₈ AuNS	C ₁₁ H ₈ AuNS
Formula Weight	383.22	383.22
Crystal System	triclinic	triclinic
Crystal Size / mm	0.114 × 0.068 × 0.015	0.114 × 0.068 × 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)
<i>α</i> / °	102.488(10)	103.379(4)
<i>β</i> / °	99.645(9)	99.477(5)
<i>γ</i> / °	96.731(9)	95.776(5)
<i>V</i> / Å ³	551.1(5)	532.54(15)
Space Group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)
<i>Z</i> value	2	2
<i>D</i> _{calc} / g·cm ⁻³	2.309	2.390
Temperature / K	298	123
2 θ _{max} / °	55.0	55.0
μ (MoK α) / cm ⁻¹	135.397	140.128
No. of Reflections	Total: 5278	Total: 5261
Measured	Unique : 2496 (<i>R</i> _{int} = 0.1115)	Unique : 2423 (<i>R</i> _{int} = 0.0943)
Residuals: <i>R</i> ₁	7.25	7.76.
(<i>I</i> > 2.00 σ (<i>I</i>)) / %		
Residuals: <i>wR</i> ₂	17.52	13.94
(All reflections) / %		
Goodness of Fit (GOF)	0.978	1.136
Maximum peak in	0.77 e ⁻	2.53 e ⁻
Final Diff. Map / Å ³		
Minimum peak in	-1.15. e ⁻	-5.17 e ⁻
Final Diff. Map / Å ³		

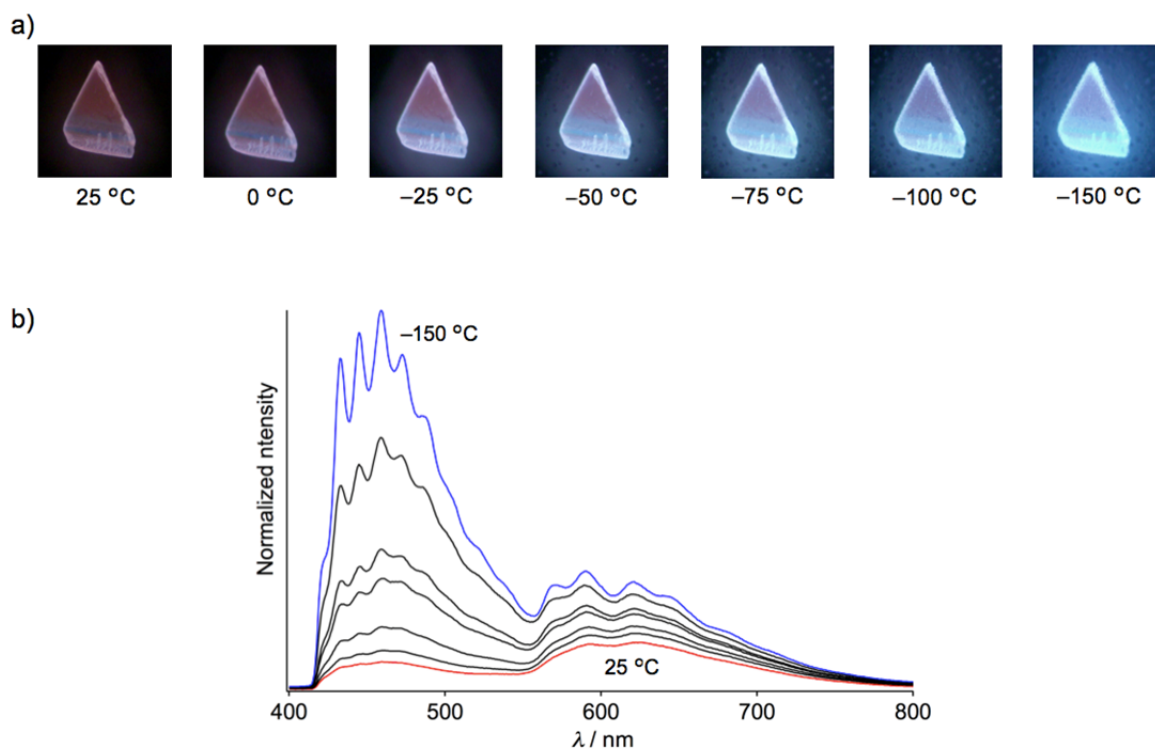


Fig. S9 a) Photographs of a crystal of **1** under UV light at various temperature. b) Emission spectral changes of single crystals of **1** at range from 25 °C to -150 °C.

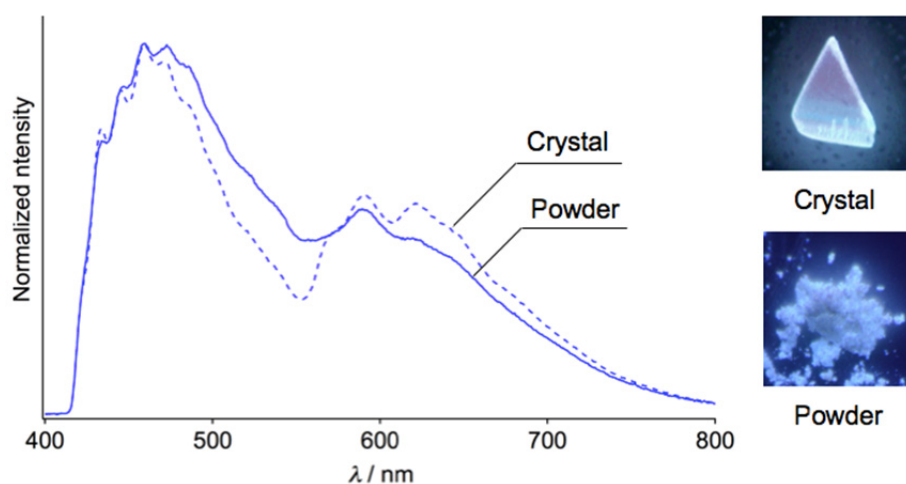


Fig. S10 Emission spectra of a powder sample of **1R_{Blue}** (-75 °C, solid line) and blue-emitting single crystal (-75 °C, dotted line) with the excitation at 365 nm. Inset shows photographs of a blue-emitting single crystal obtained by recrystallization (-75 °C, upper) and a powder sample of **1R_{Blue}**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

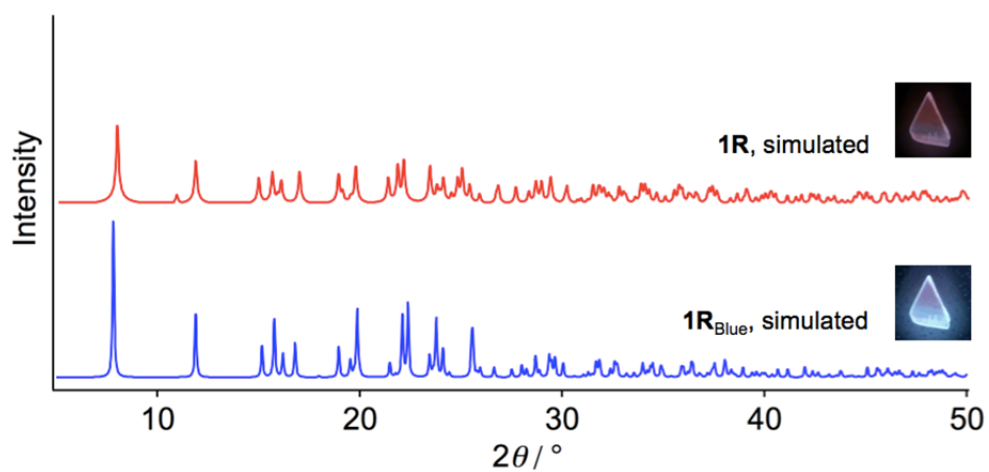


Fig. S11 Simulated powder XRD patterns derived from the red- and blue-emitting single crystals, corresponding to **1R** and **1R_{Blue}**, respectively.

8. DSC analysis of 1R within the low temperature

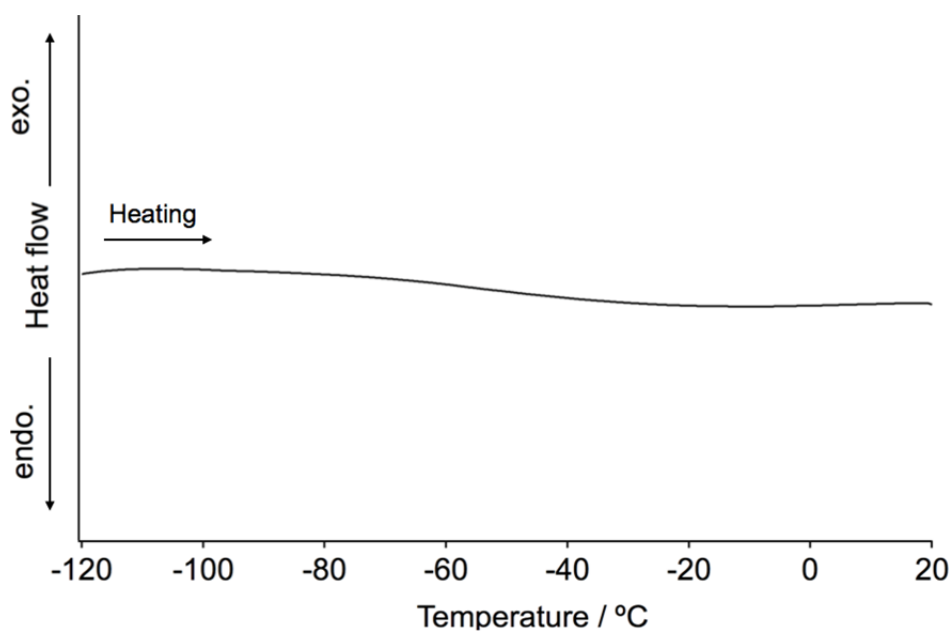


Fig. S12 DSC analysis of **1** ranging from $-120\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Because of limitation of our instrument, we can not perform DSC analyses of samples during cooling. Thus, this measurement is performed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

9. Powder XRD analyses

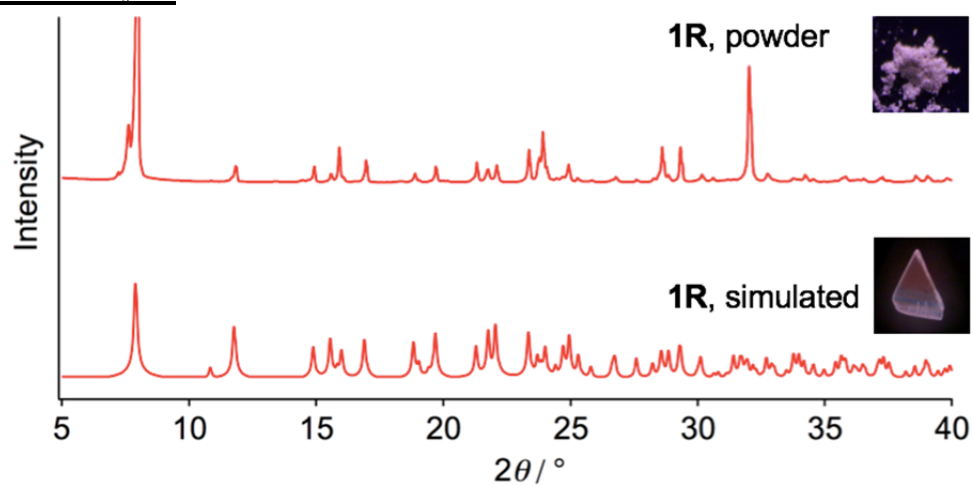


Fig. S13 Powder XRD pattern of **1R** at room temperature (upper pattern) and simulated powder XRD pattern of the red-emitting single crystal of **1** (lower pattern).

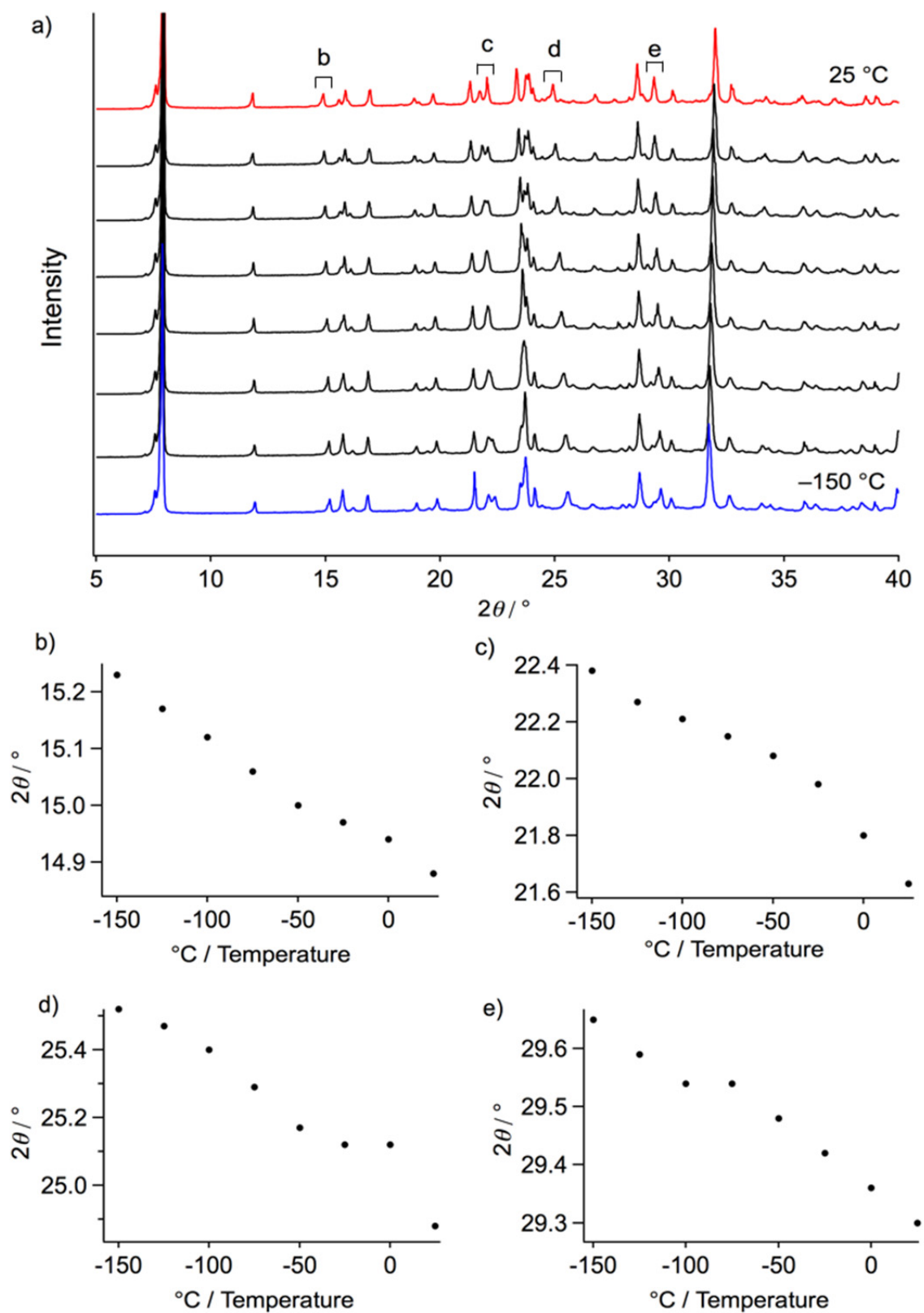


Fig. S14 a) Temperature-dependent powder XRD patterns of **1**. Measurement temperature: 25, 0, -25, -50, -75, -100, -150 °C. b-e) Plots of a position of specific peaks with respect to temperature, indicating gradual peak shifts.

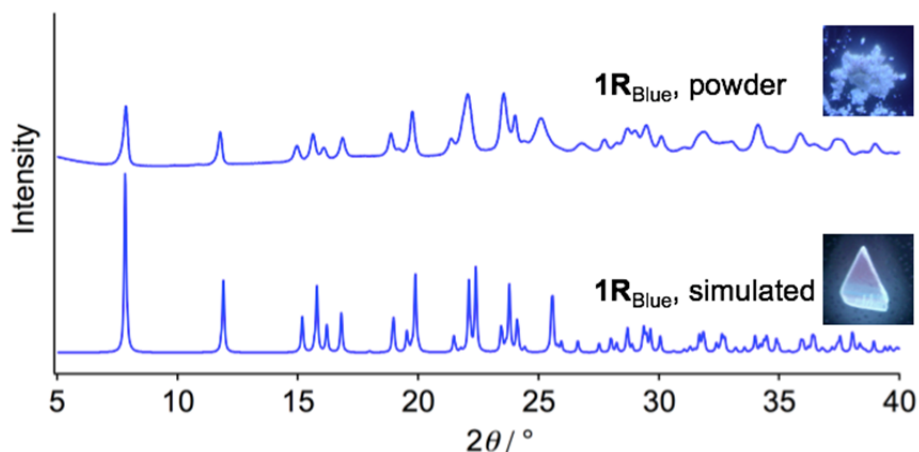


Fig. S15 Powder XRD pattern of **1R_{Blue}** at $-150\text{ }^{\circ}\text{C}$ (upper pattern) and simulated powder XRD pattern of the blue-emitting single crystal of **1** (lower pattern).

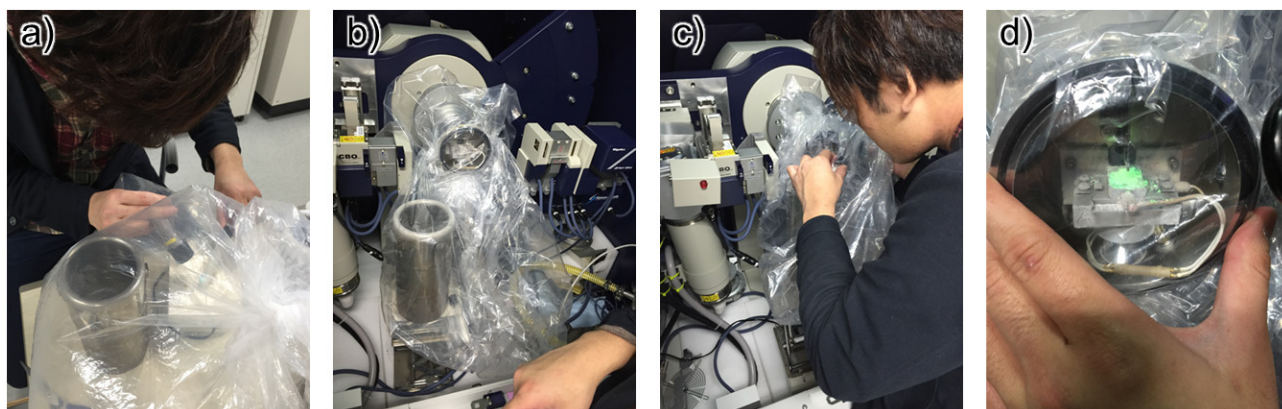


Fig. S16 Photographs when **1G** samples for powder XRD analyses were prepared.

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**→**1R_{Blue}**), before stirring was applied for 3 h (**1R_{Blue}**→**1G**). The sample stage of the powder XRD apparatus was also covered with a nitrogen-filled plastic bag and cooled to $-150\text{ }^{\circ}\text{C}$ (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

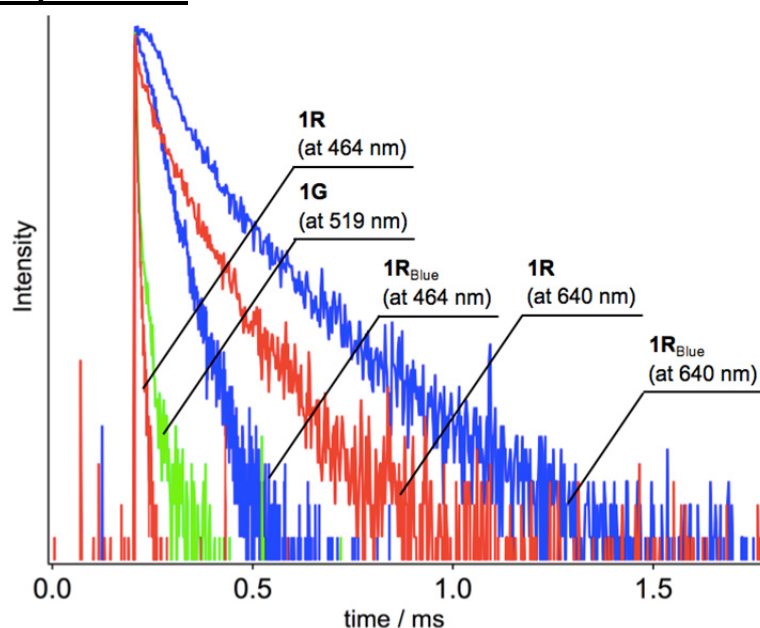


Fig. S17 Emission decay profiles of **1R**, **1R_{Blue}**, and **1G** with the excitation at 370 nm. Monitored emission wavelengths are 464 nm for **1R** and **1R_{Blue}**, 519 nm for **1G**, and 640 nm for **1R** and **1R_{Blue}**.

Table S2. Summary of photophysical data of **1**.

	χ / -	$\tau_{av}^{b,c}$ / μs	τ_1 / μs (A / -)	τ_2 / μs (A / -)	τ_3 / μs (A / -)
1R (at 640 nm) ^a	1.11	83	1.4 (0.75)	27.2 (0.10)	99.1 (0.15)
1R (at 464 nm) ^a	1.38	1	0.50 (0.61)	1.73 (0.39)	—
1R_{Blue} (at 640 nm) ^a	1.30	127	0.52 (0.62)	65.3 (0.30)	203.5 (0.08)
1R_{Blue} (at 464 nm) ^a	1.26	41	0.43 (0.77)	31.0 (0.16)	54.9 (0.08)
1G (at 519 nm) ^a	^d	^d	^d	^d	^d

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

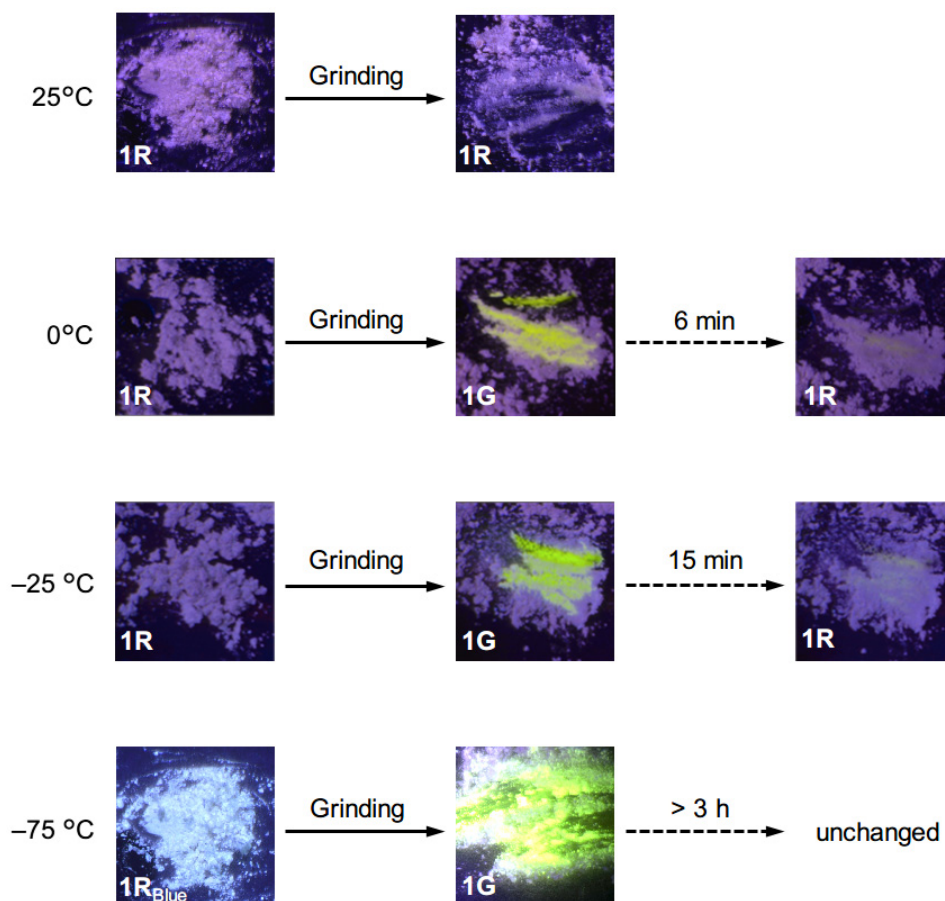
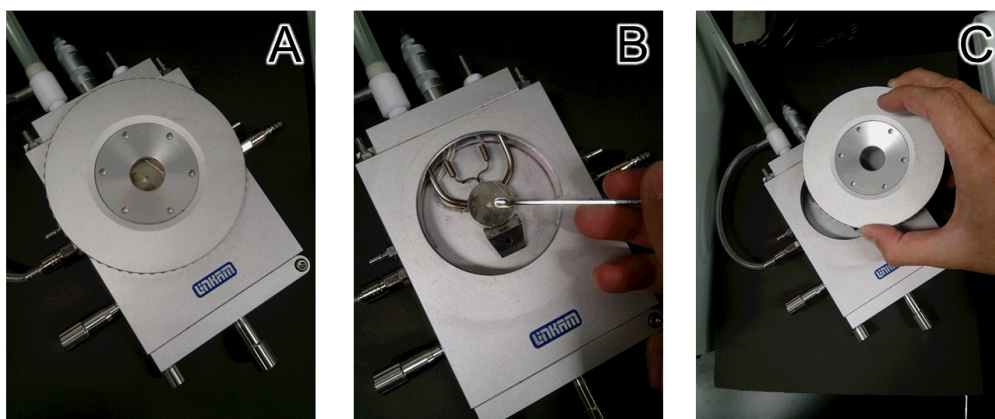


Fig. S18 Photographs of solid samples of **1** taken under UV light when mechanically stimulated at various temperature. It should be note that we also confirmed that **1G** is intact for more than one day at $-78\text{ }^{\circ}\text{C}$, when **1G** was obtained by mechanical stimulation with a stirring bar in a test tube, where the sample can be kept easily at $-78\text{ }^{\circ}\text{C}$ 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 $-75\text{ }^{\circ}\text{C}$, 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

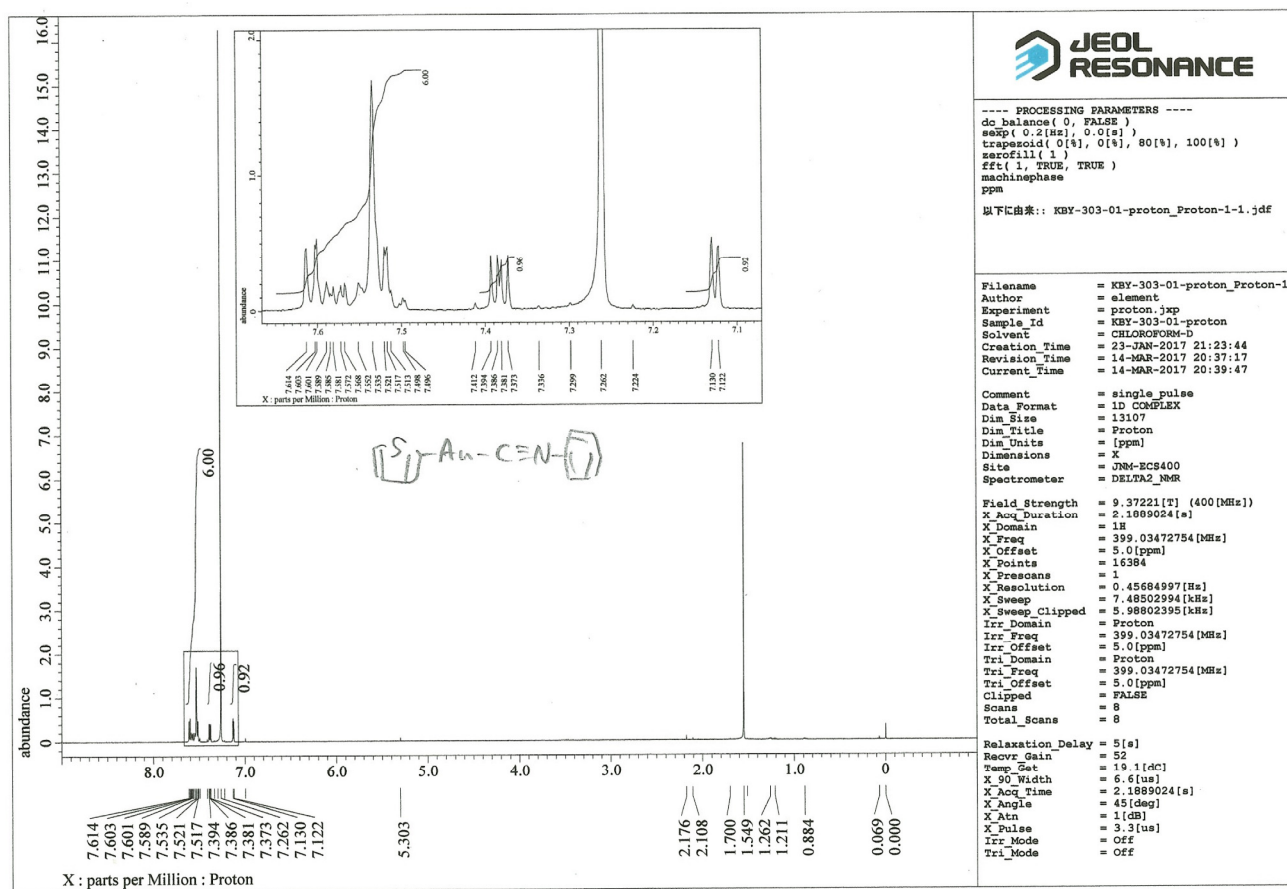


Fig. S19 ¹H NMR spectrum of **1** dissolved in CDCl₃.

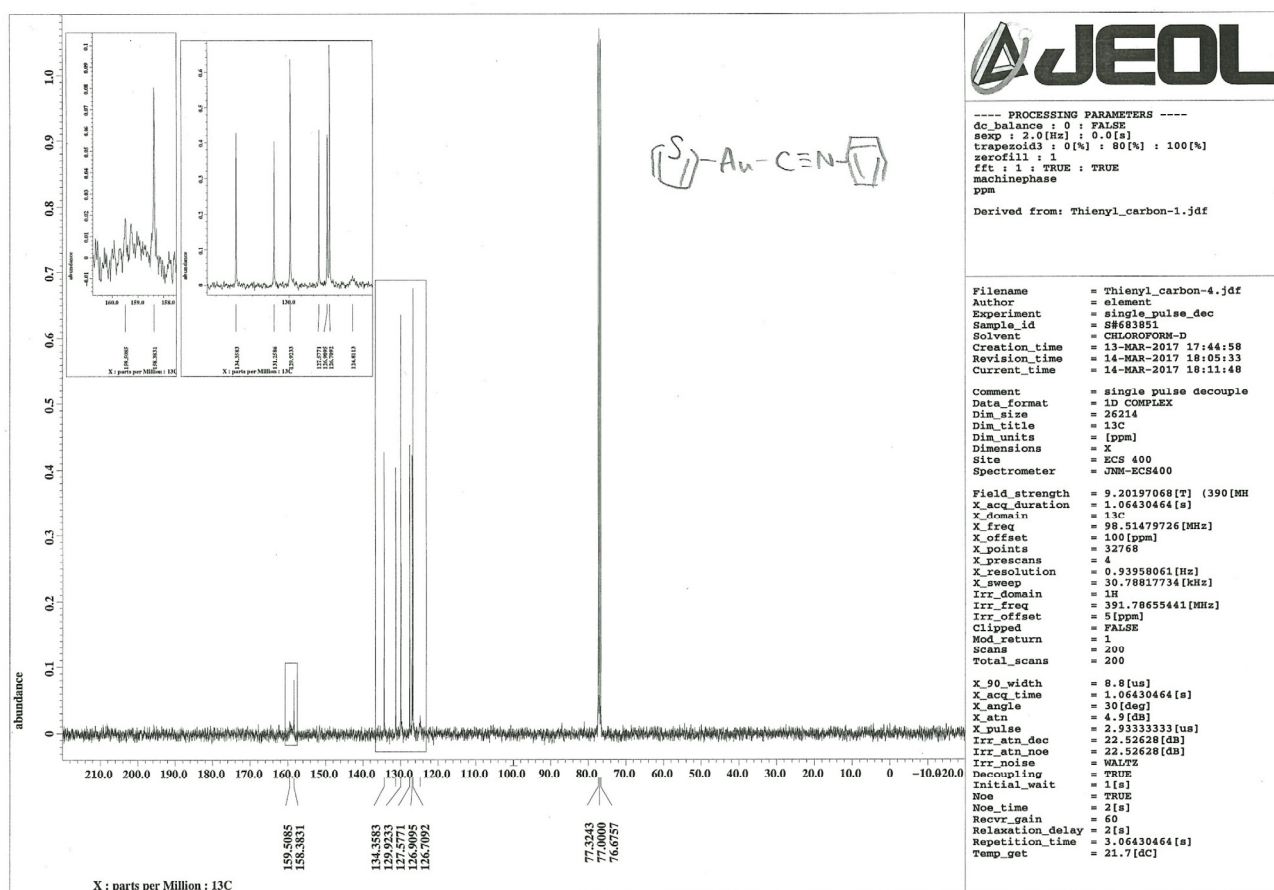


Fig. S20 ^{13}C NMR spectrum of **1** dissolved in CDCl_3 .

12. References

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- http://www.ccdc.cam.ac.uk/free_services/mercury/downloads/Mercury_3.0/