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Electronic Supplementary Information

A meta-diisocyanide benzene-based aryl gold isocyanide complex exhibiting multiple solid-state molecular arrangements and luminescent mechanochromism

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Contents

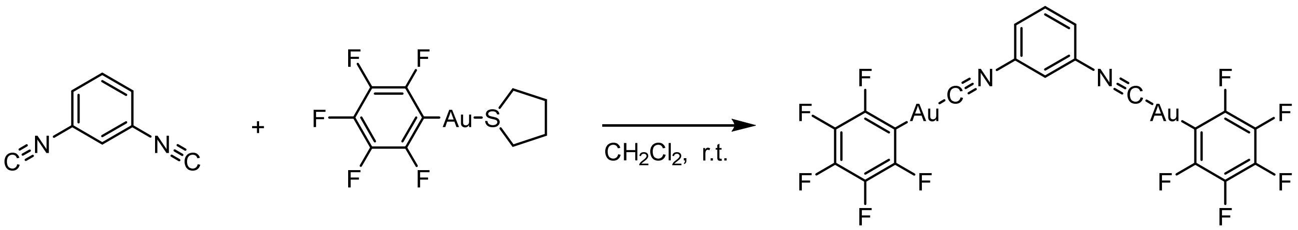
1. General

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). ^{1}H NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz) spectrometer and chemical shifts were reported in ppm (δ) with the signal of tetramethylsilane as internal standard respectively. High resolution mass spectra were recorded at the Global Facility Center at Hokkaido University. Emission spectra were recorded on a Hitachi F-7000 spectrometer and Olympus fluorescence microscope BX51 equipped with Hamamatsu photonics multichannel analyzer PM-12. Absorption spectra were recorded on a Hitachi U-2910 spectrometer. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 or RICOH CX1 digital cameras. Thermal gravimetric analysis profiles were recorded on Bruker TG-DTA2010SAT and SII EXSTAR 6000. Powder diffraction data were recorded at on a Rigaku SmartLab diffractometer with Cu-K_α radiation and D/teX Ultra detector.

Single crystal structure 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-2013.[1]

2. Synthesis

A mixture of pentafluorophenyl(tetrahydrothiophen)gold(I)[2] (800 mg, 1.77 mmol) and 1,3-diisocyanobenzene[3] (108 mg, 0.84 mmol) was stirred in CH_2Cl_2 (27 mL) for 4 h under air at room temperature. After the reaction completion was monitored by TLC analysis, the solvent was removed with a rotary evaporator under a reduced pressure. The residues are washed with methanol, which gave analytically pure **2** as yellow solid (3.677 g, 9.71 mmol, 97% yield). ^{1}H NMR (400 MHz, acetone-d_6, δ): 8.01 (t, 1H, J = 8.4 Hz), 8.27, (d, J = 8.4 Hz, 2H), 8.59 (s, 1H). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{20}H_4Au_2F_{10}N_2Na$, 878.9444; found, 878.9444. This compound exhibits poor solubility in common organic solvents (for example, maximum solubility in acetone is 1.0 mg/mL); therefore, ^{13}C NMR spectroscopy can not be evaluated.



3. Preparation of Solid Samples of 2a–2g

Preparation of 2a: **2a** was obtained by slow crystallization. Typically, a solution of **2** (2 mg) in 5 mL of ethyl acetate was transferred to a petri dish. After standing this solution for a week at 4 °C, blue-emitting crystals **2a** were formed in the remaining solution.

Preparation of 2b: **2b** was obtained by slow crystallization. Typically, a solution of **2** (2 mg) in 2 mL of THF was transferred to a petri dish. After standing this solution for a week at 4 °C, all THF is evaporated and blue-emitting crystals **2b** can be obtained.

Preparation of 2c: **2c** was obtained by slow crystallization. Typically, a solution of **2** (2 mg) in 2 mL of THF in a vial was heated at 80 °C for ~15 min. After evaporated all THF, deep green-emitting crystals **2c** can be obtained.

Preparation of 2d: **2d** was obtained by very rapid evaporation. Typically, for a suspension of **2** (2 mg) in 20 mL of MeOH in a vial, the solvent was evaporated by a rotary evaporator, which gave green-emitting semicrystalline powder **2d** quantitatively.

Preparation of 2e: **2e** was obtained by very rapid evaporation. Typically, for a solution of **2** (2 mg) in 20 mL of Et_2O in a vial, the solvent was evaporated by a rotary evaporator, which gave green-emitting semicrystalline powder **2e** quantitatively.

Preparation of 2f: **2f** was obtained by very rapid evaporation. Typically, for a solution of **2** (2 mg) in 20 mL of ethyl acetate in a vial, the solvent was evaporated by a rotary evaporator, which gave green-emitting semicrystalline powder **2f** quantitatively.

Preparation of 2g: **2g** was obtained by very rapid evaporation. Typically, for a solution of **2** (2 mg) in 20 mL of THF in a vial, the solvent was evaporated by a rotary evaporator, which gave green-emitting semicrystalline powder **2g** quantitatively.

4. Optical Properties of 2 in Solution

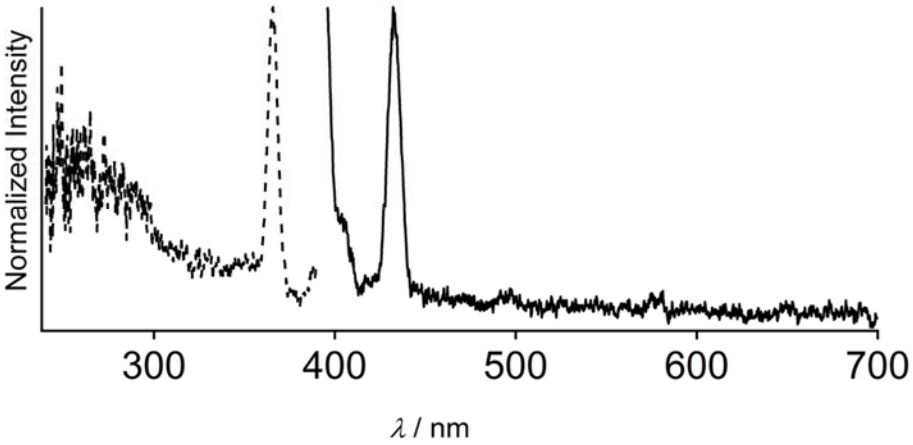


Fig. S1. Excitation (dashed line) and emission spectra (solid line) of **2** in CH_2Cl_2 at room temperature. λ_{ex} = 365 nm; λ_{em} = 414 nm; [**2**] = 1.00×10^{-4} M.

5. Data for Single Crystal X-ray Structural Analyses

Table S1. Summary of X-ray crystallographic data for **2a**, **2b** and **2c**

Polymorph	**2a**	**2b**	**2c**
CCDC Number	1820938	1820947	1822803
Empirical Formula	$C_{20}H_4Au_2F_{10}N_2(C_{10}H_{20}O_5)$	$C_{20}H_4Au_2F_{10}N_2(C_8H_{16}O_2)$	$C_{20}H_4Au_2F_{10}N_2(C_4H_8O)$
Formula Weight	1076.45	1000.40	928.29
Crystal System	triclinic	monoclinic	triclinic
Crystal Size / mm	0.248 × 0.149 × 0.123	0.3798 × 0.2668 × 0.142	0.133 × 0.101 × 0.042
a / Å	10.5053(14)	8.4401(7)	10.5280(9)
b / Å	11.0003(18)	17.3470(13)	11.5191(11)
c / Å	14.675(2)	19.5954(15)	11.8538(11)
α / °	79.575(5)	90	70.006(2)
β / °	87.376(4)	98.181(2)	70.754(2)
γ / °	86.965(5)	90	67.223(3)
V / Å^3	1664.4(4)	2839.8(4)	1212.85(19)
Space Group	P-1 (#2)	$P2_1/n$ (#14)	P-1 (#2)
Z value	2	4	2
D_{calc} / g cm^{-3}	2.148	2.340	2.542
Temperature / K	123	123	123
$2\theta_{max}$ / °	55.0	52.0	50.1
μ (MoK$_\alpha$) / cm^{-1}	89.323	104.531	122.236
No. of Reflections Measured	Total: 16335 Unique: 7488 (R_{int} = 0.1532)	Total: 23997 Unique: 5575 (R_{int} = 0.1579)	Total: 9607 Unique: 4294 (R_{int} = 0.0891)
No. of Observations (All reflections)	7488	5575	4294
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0757	0.0623	0.0689
Residuals: wR_2 (All reflections)	0.2389	0.1544	0.2219
Goodness of Fit Indicator (GOF)	1.039	0.990	0.979
Maximum peak in Final Diff. Map / Å^3	2.18 e$^-$	2.30 e$^-$	2.61 e$^-$
Minimum peak in Final Diff. Map / Å^3	–3.50 e$^-$	–3.26 e$^-$	–3.82 e$^-$

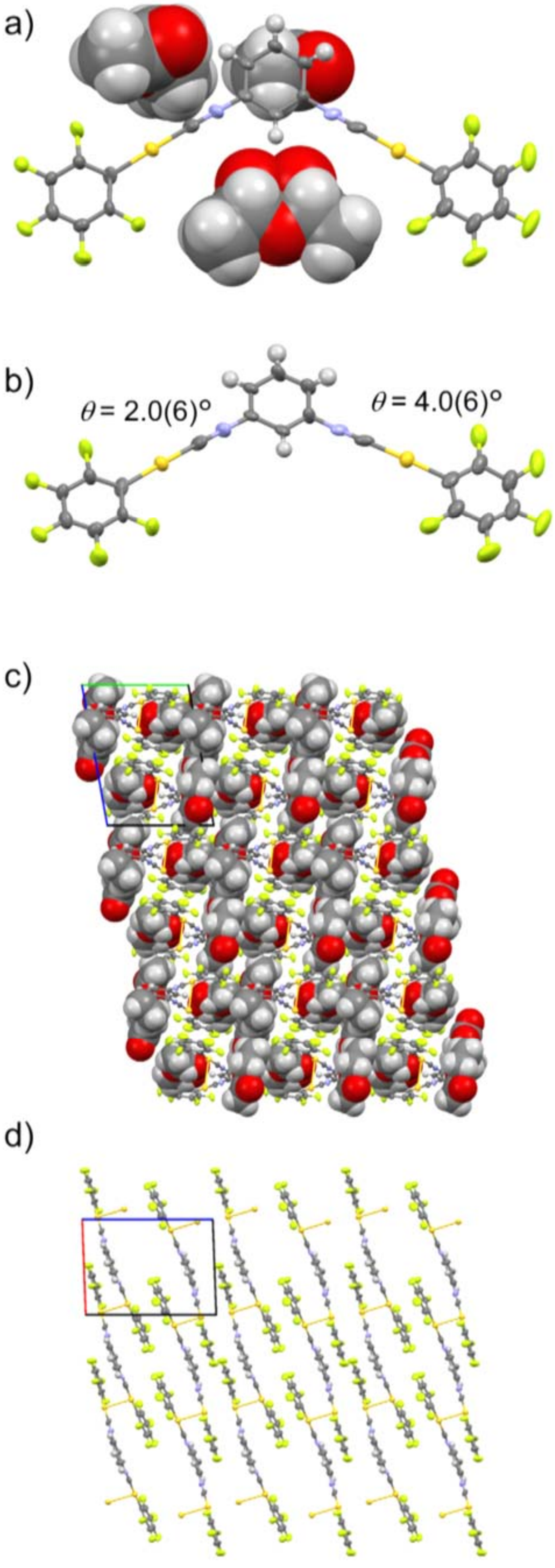


Fig. S2. Single-crystal structure of **2a**.

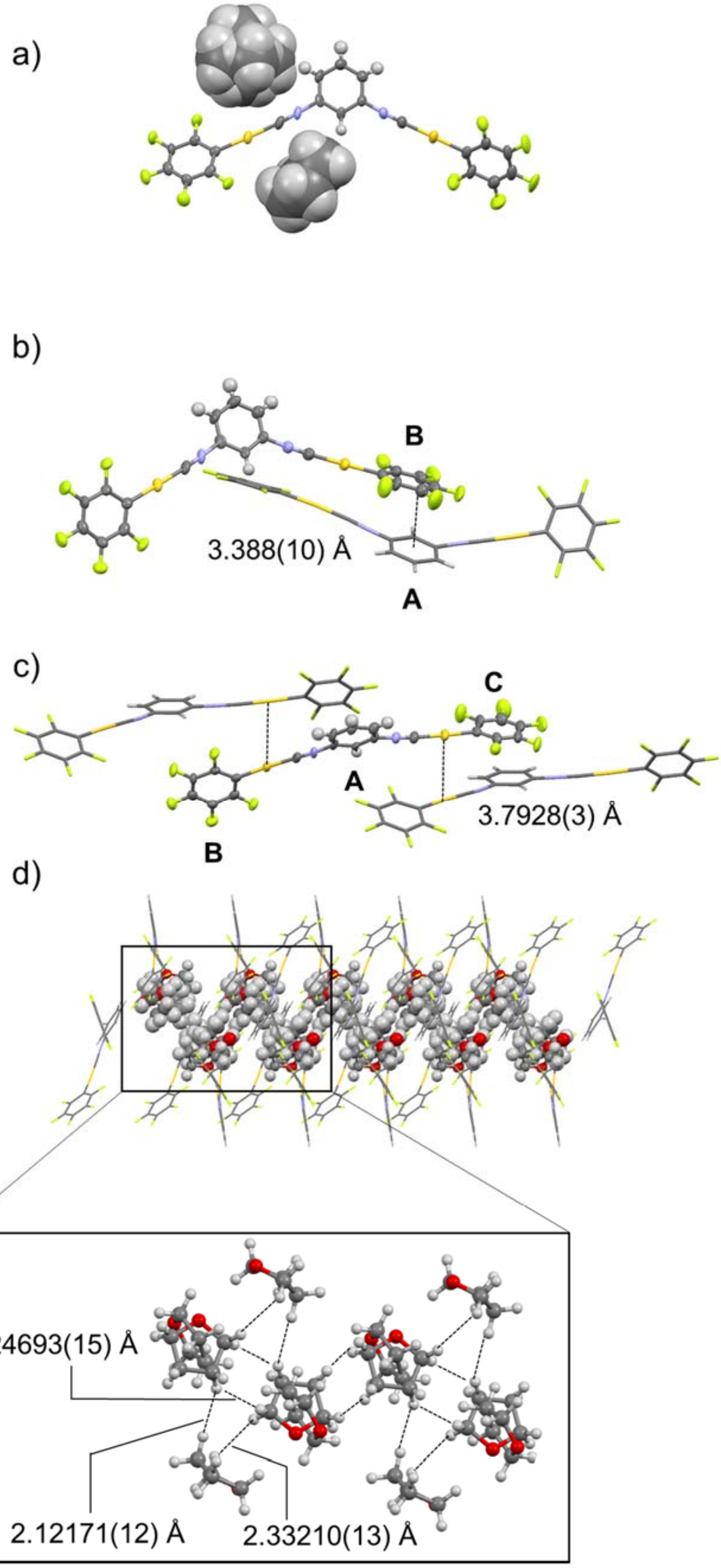


Fig. S3. Single-crystal structure of **2b**.

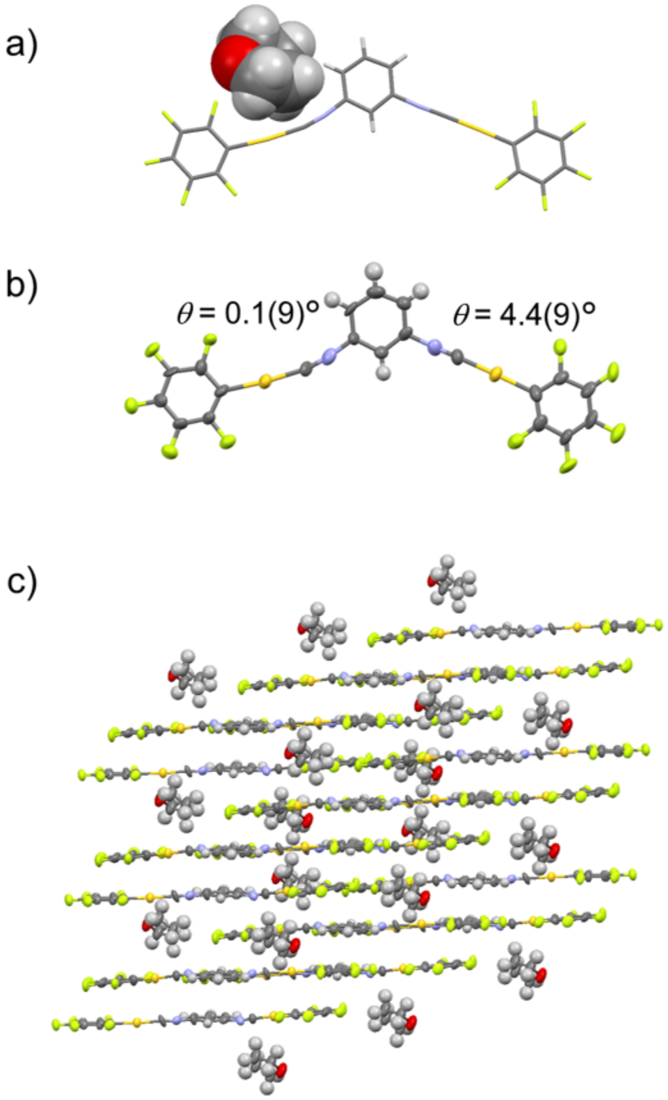


Fig. S4. Single-crystal structure of **2c**.

6. A Yellow-Emitting Solid Sample of 2

Preparation of yellow-emitting solid sample of 2: This solid sample was obtained by very rapid crystallization. Typically, for a homogeneous solution of **2** (2 mg) in 20 mL of dichloromethane in a vial, all solvents were evaporated by a rotary evaporator and this yellow-emitting semicrystalline powder were obtained quantitatively.

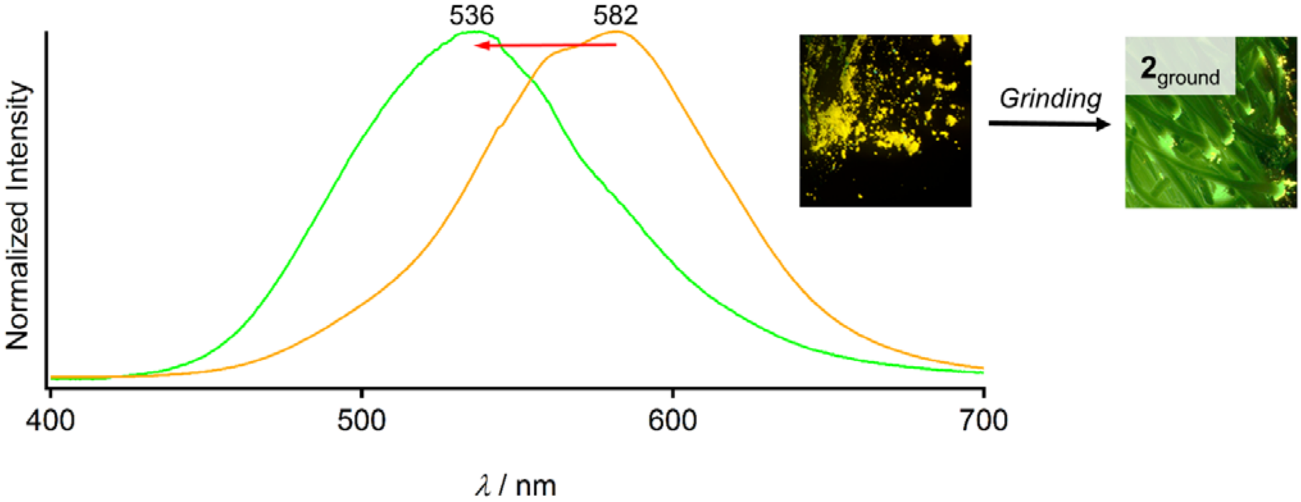


Fig. S5. Emission spectra of the yellow-emitting solid sample **2** obtained by the above procedure recorded before and after mechanical stimulation (λ_{ex} = 365 nm). A red allow indicates the change upon mechanical stimulation. Inset shows photographs of the yellow-emitting solid sample **2** before and after mechanical stimulation taken under UV light.

7. Comparison of the Emission Spectra of 2a–2g and 2_{ground}

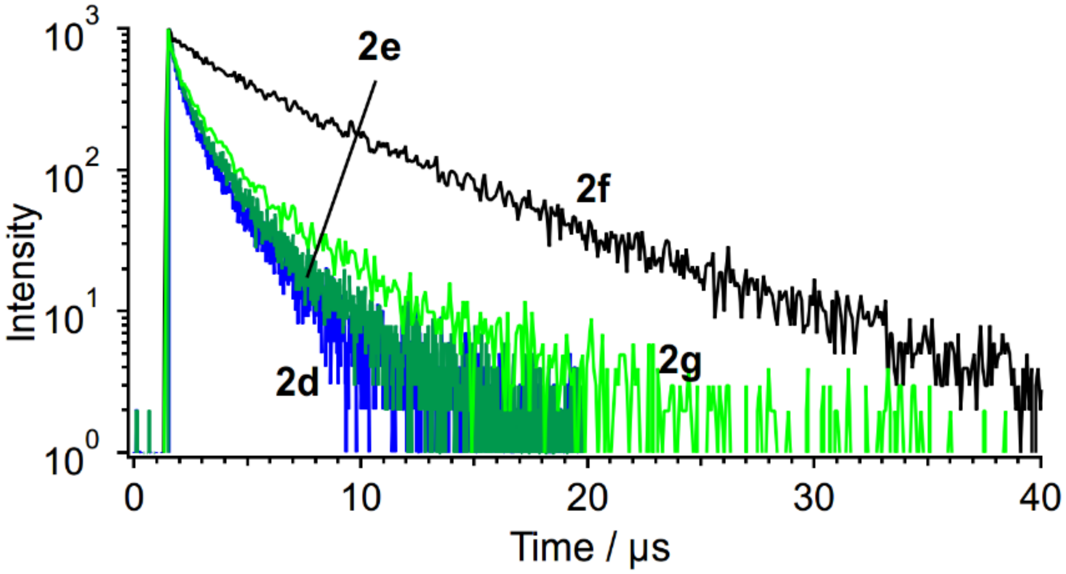


Fig. S6. Emission decay profiles of **2d**–**2g** excited at 365 nm. Monitoring emission wavelengths are 500 nm.

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

	τ_{av}[a,b,c]/ µs	τ_1 / µs (A / -)	τ_2 / µs (A / -)
2d	0.870	0.393 (0.65)	1.76 (0.35)
2e	1.03	0.455 (0.64)	2.02 (0.36)
2f	4.94	0.189 (0.35)	6.58 (0.65)
2g	1.44	0.791 (0.76)	3.57 (0.24)

[a]: Monitored emission wavelength: 500 nm. [b]: τ_{av} is defined as: $\Sigma(A_n\tau_n) / \Sigma(A_n)$. [c]: $\lambda_{ex} = 370$ nm.

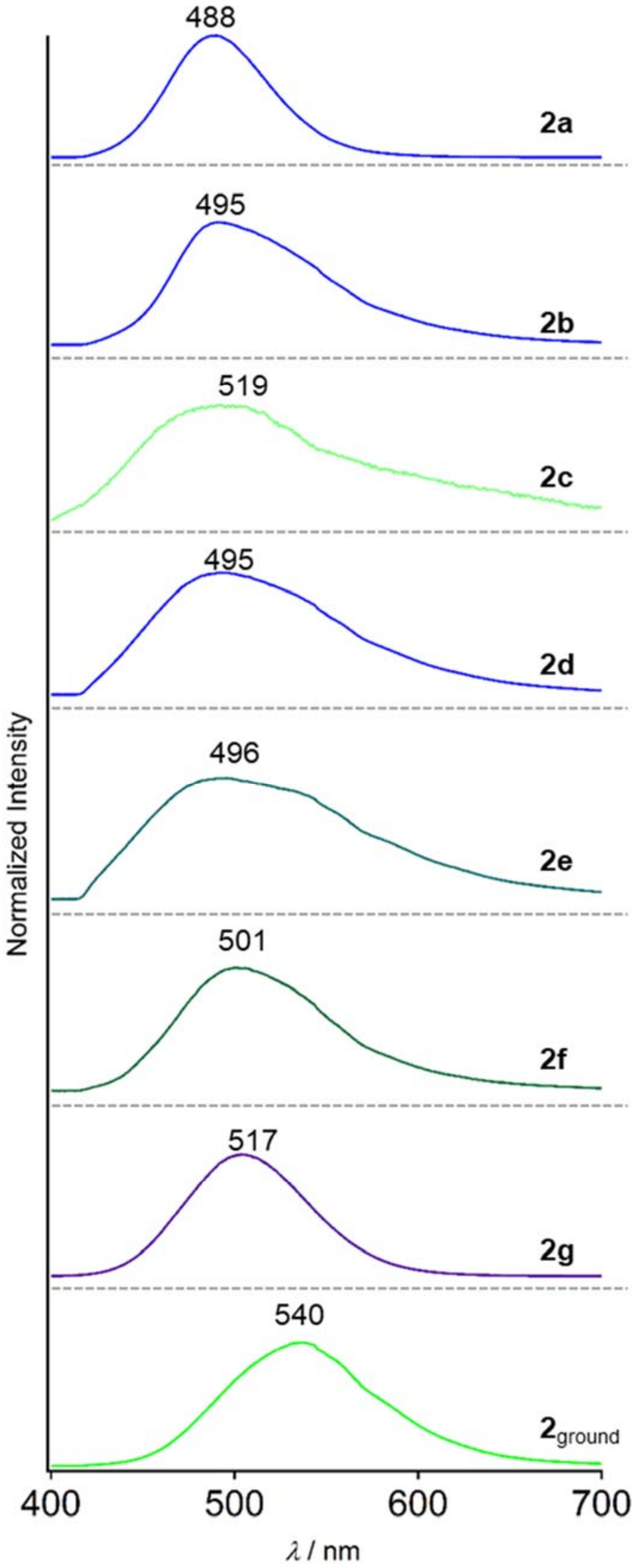


Fig. S7. Emission spectra of **2a**–**2g** and **2**$_{\text{ground}}$ excited at 365 nm.

8. NMR and TGA Measurements

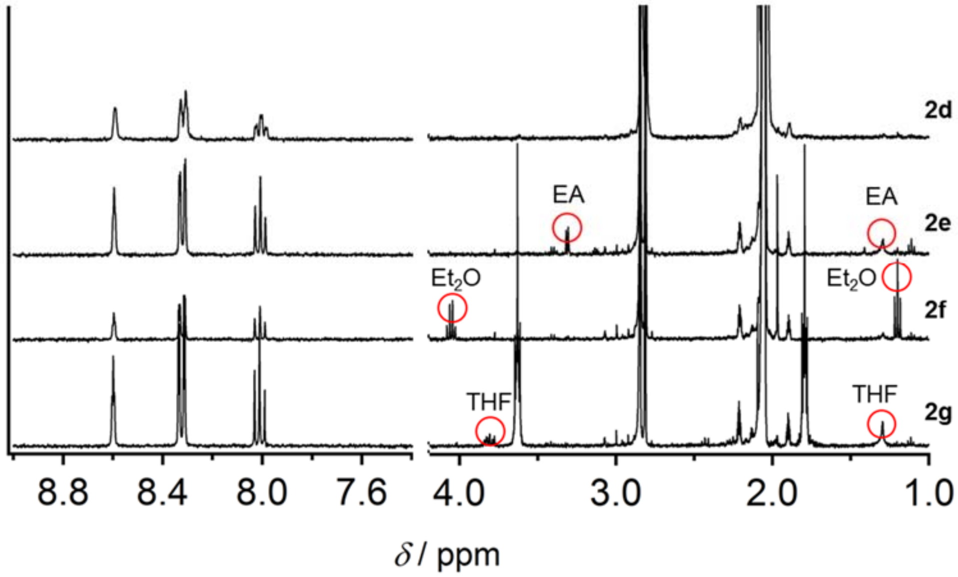


Fig. S8. ^{1}H NMR spectra of **2d**–**2g** in acetone-d_6. All samples are dried under vacuum for ~2 h before dissolution in acetone-d_6.

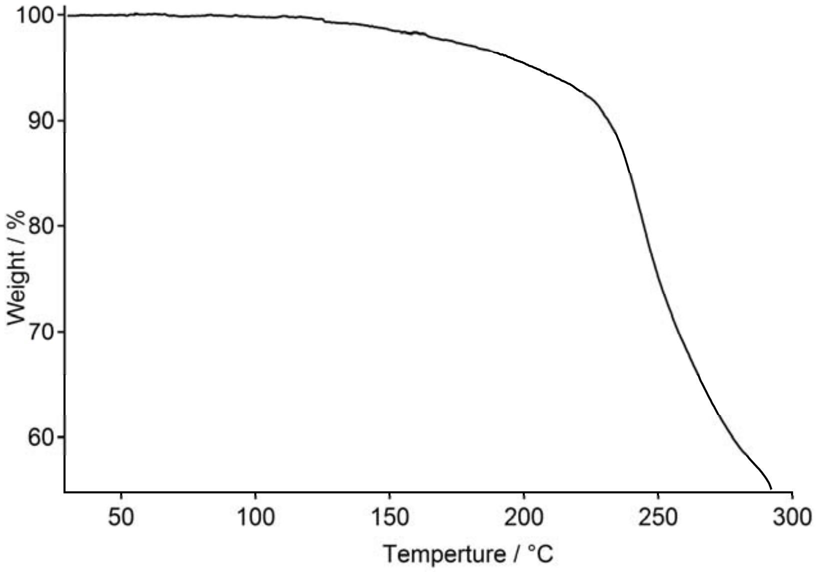


Fig. S9. TGA profiles of **2d**. A heating rate is 5 °C/min.

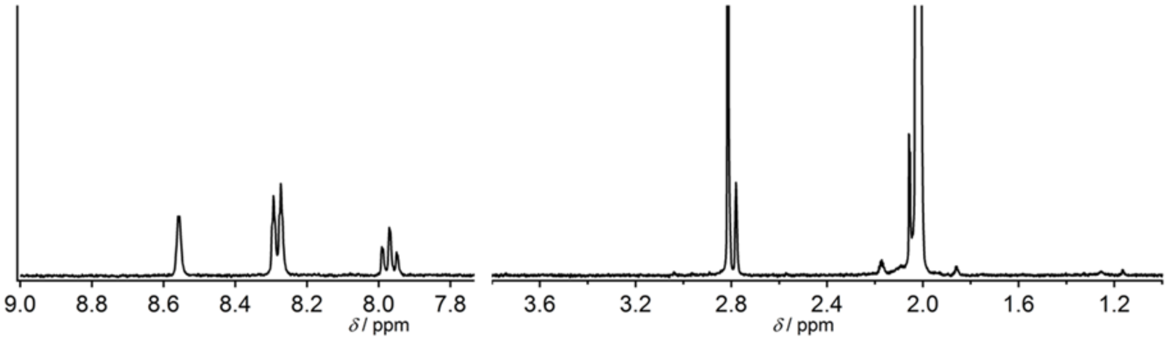


Fig. S10. ^{1}H NMR spectrum of ground powder $\mathbf{2}_{\mathrm{ground}}$ in acetone-d_6.

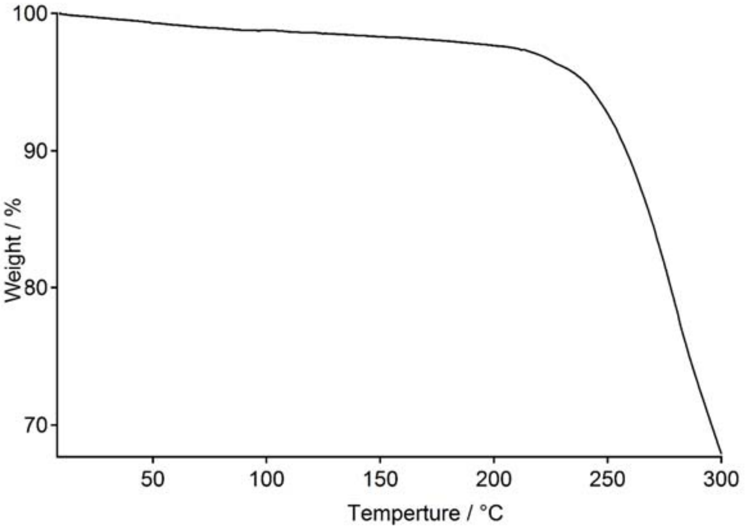
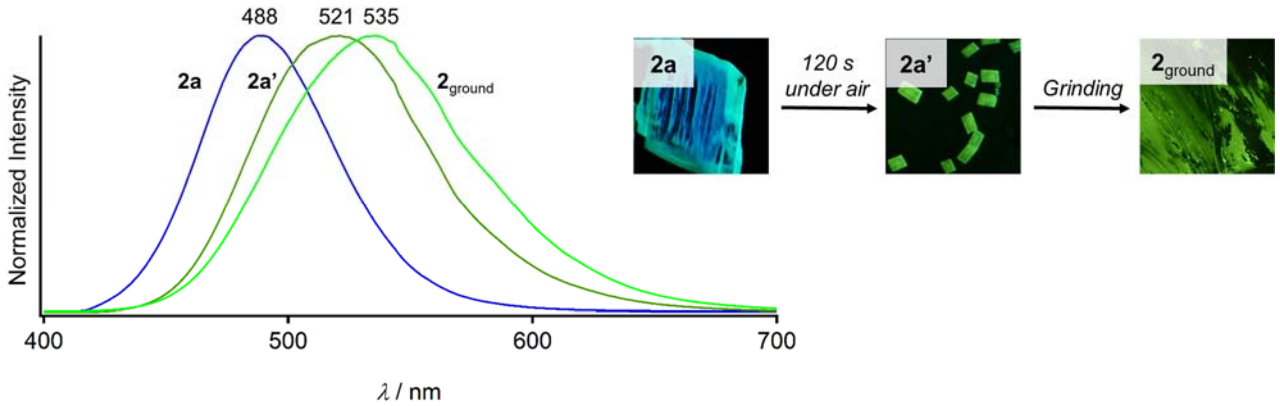
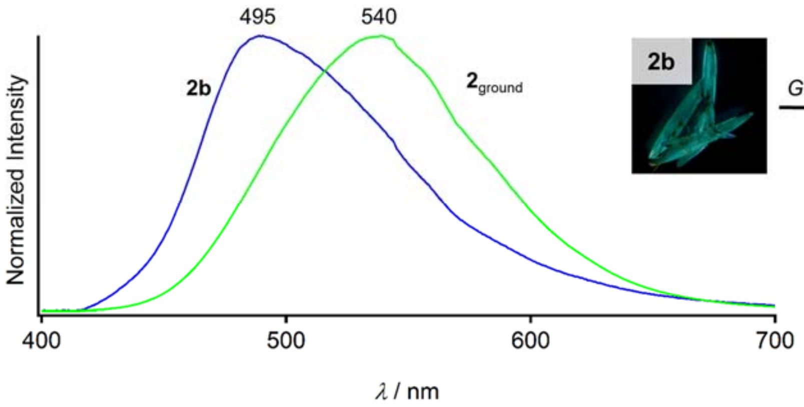
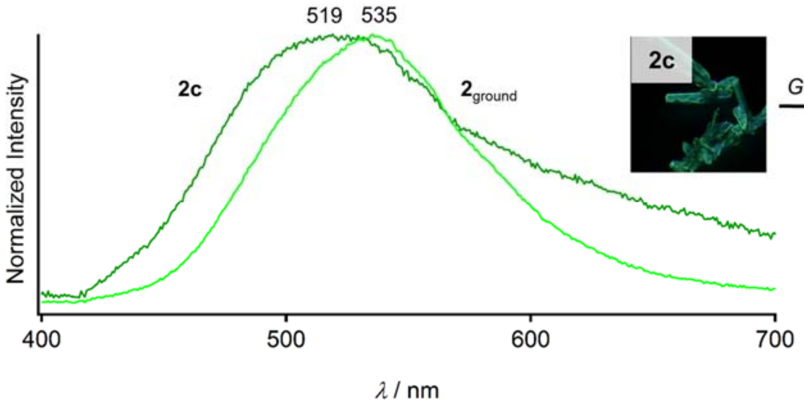


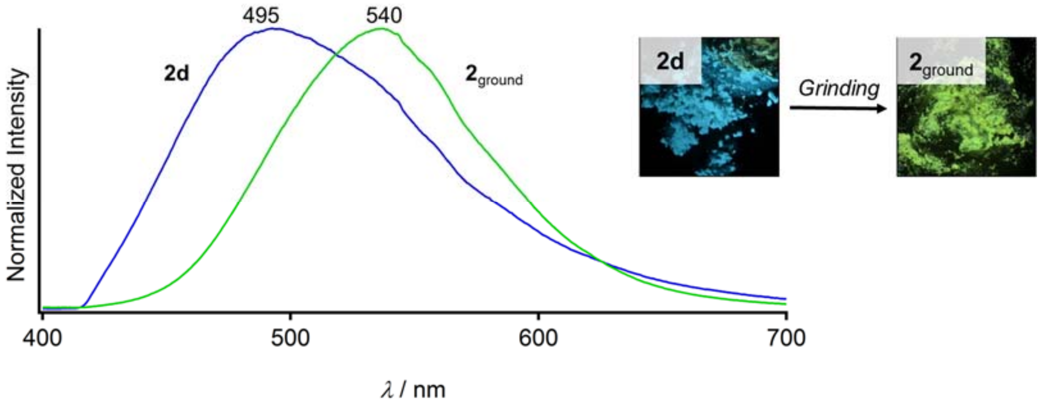
Fig. S11. TGA profiles of powder samples of $\mathbf{2}_{\mathrm{ground}}$ which are obtained from **2b** by mechanical stimulation. A heating rate is 5 °C/min.

9. Luminescent Mechanochromism of 2a–2g









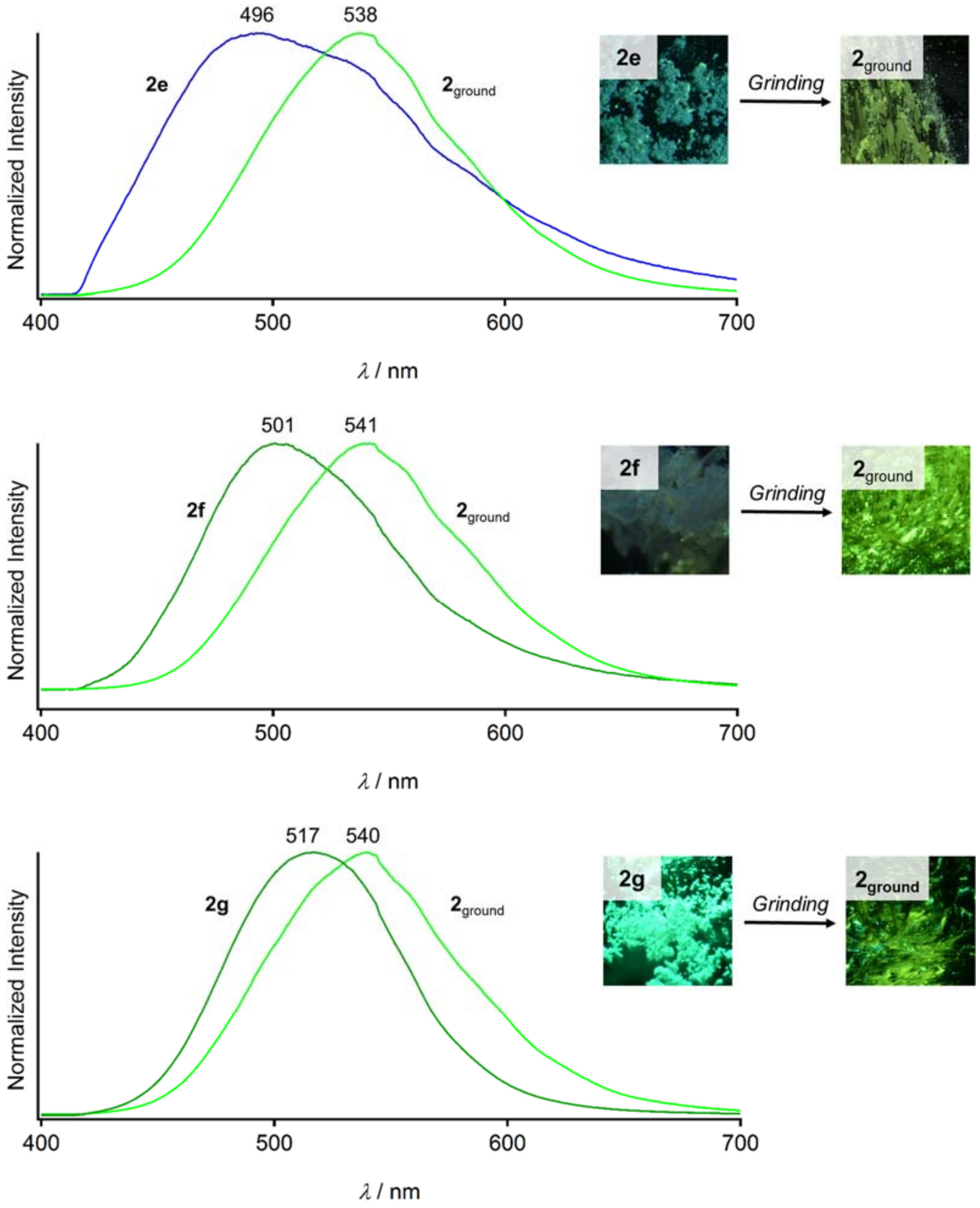


Fig. S12. Emission spectra (λ_{ex} = 365 nm) and photographs (insets, λ_{ex} = 365 nm) of **2a–2g** recorded before and after mechanical stimulation.

10. Reversible Phase Transitions of 2d

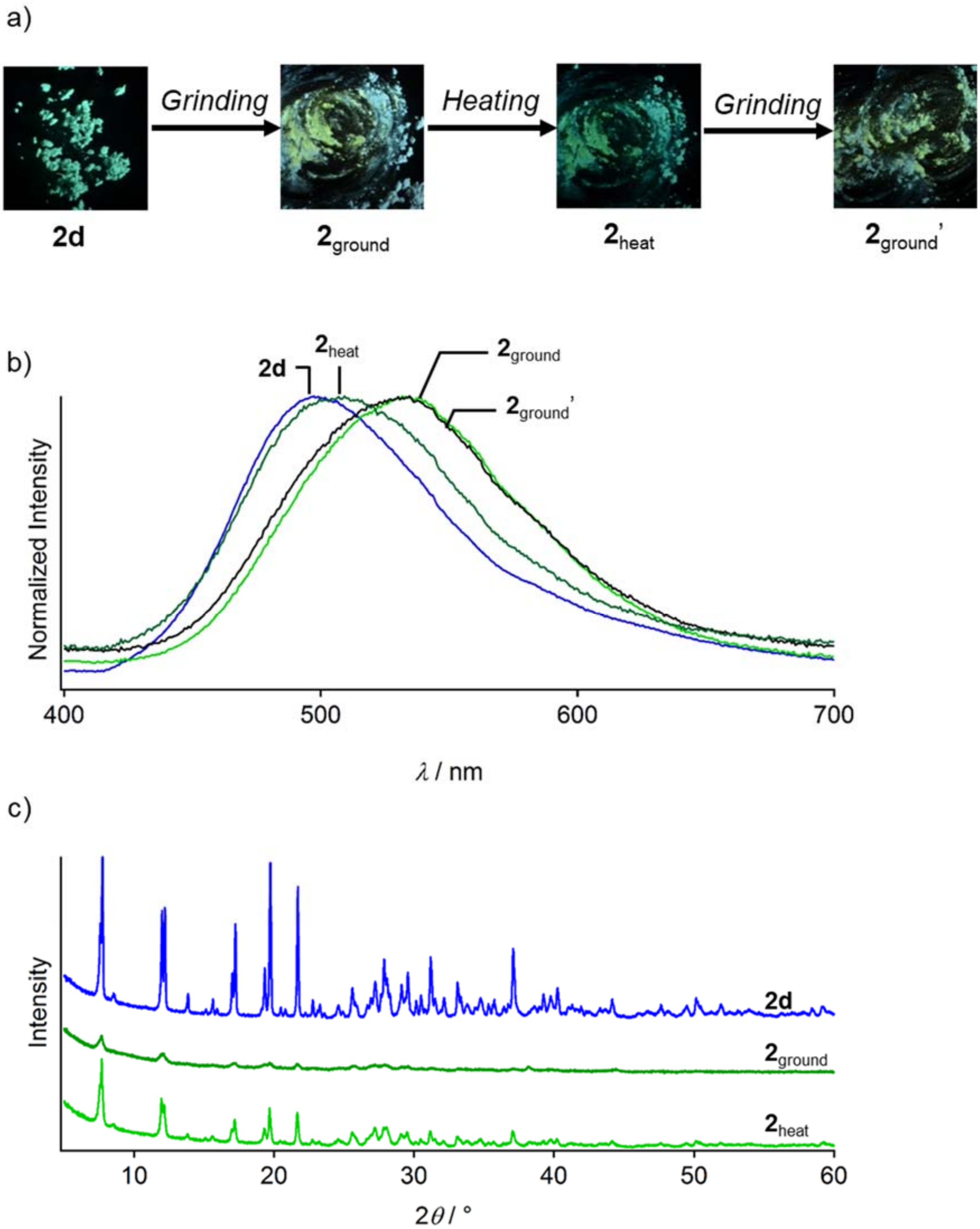


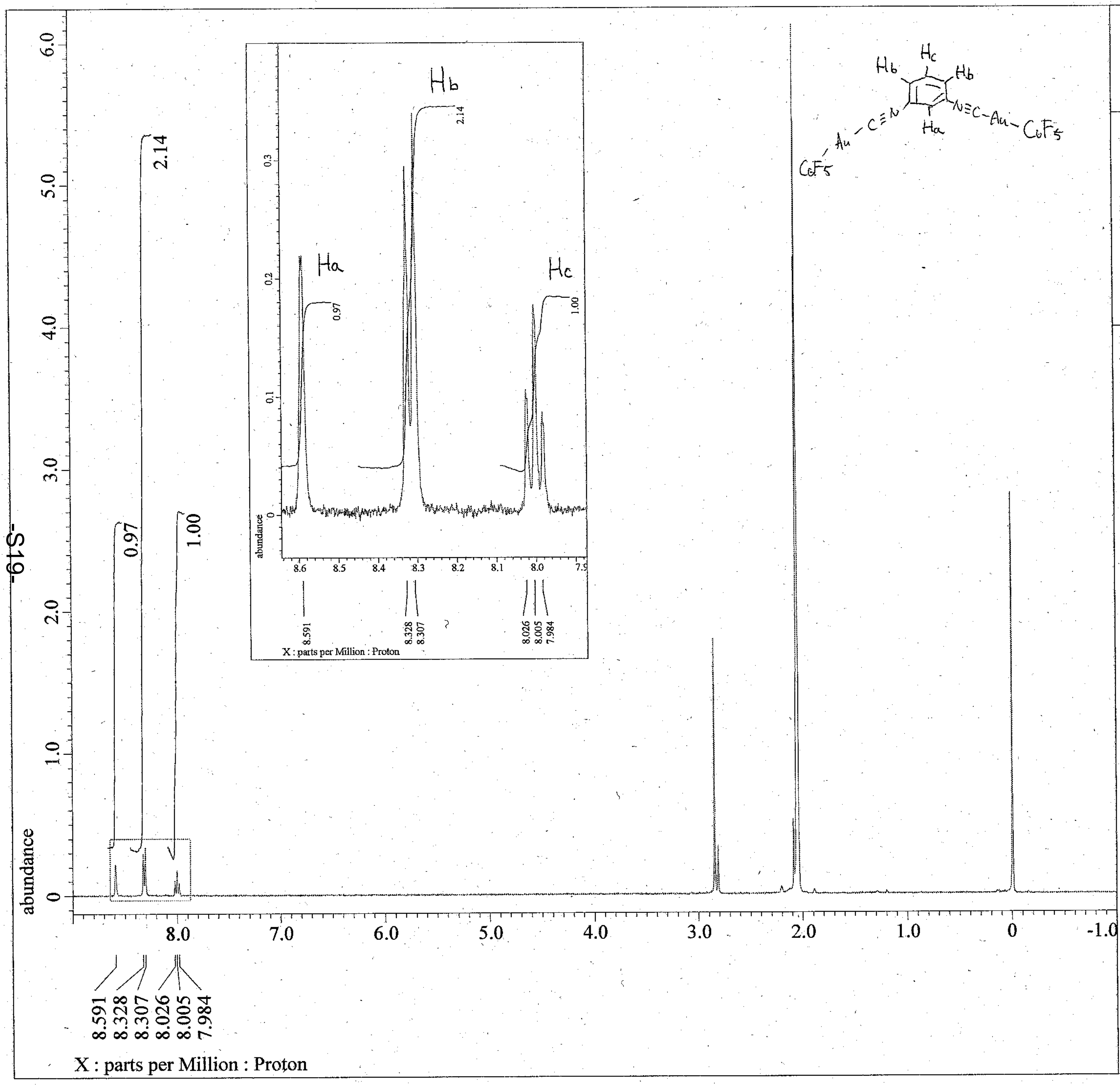
Fig. S13. a) Photographs (λ_{ex} = 365 nm), b) emission spectra (λ_{ex} = 365 nm), and powder XRD patterns of the **2d** which were recorded after applying various external stimulation.

11. References

(1) Sheldrick, G. M. SHELXL-2013, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 2013

(2) R. Uson, A. Laguna, M. Laguna, *Inorg. Synth.*, 1989, **26**, 85–91.

(3) A. Efraty, I. Feinstein, J. L. Wackerle, *Organomet. Chem.* 1981, **220**, 333–340.



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