Tunable mechanochromic luminescence via surface protonation of pyridyl-substituted imidazole crystals

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Table of contents

1. Differential scanning calorimetry (DSC) measurements

*DSC thermograms of **1** and **2***

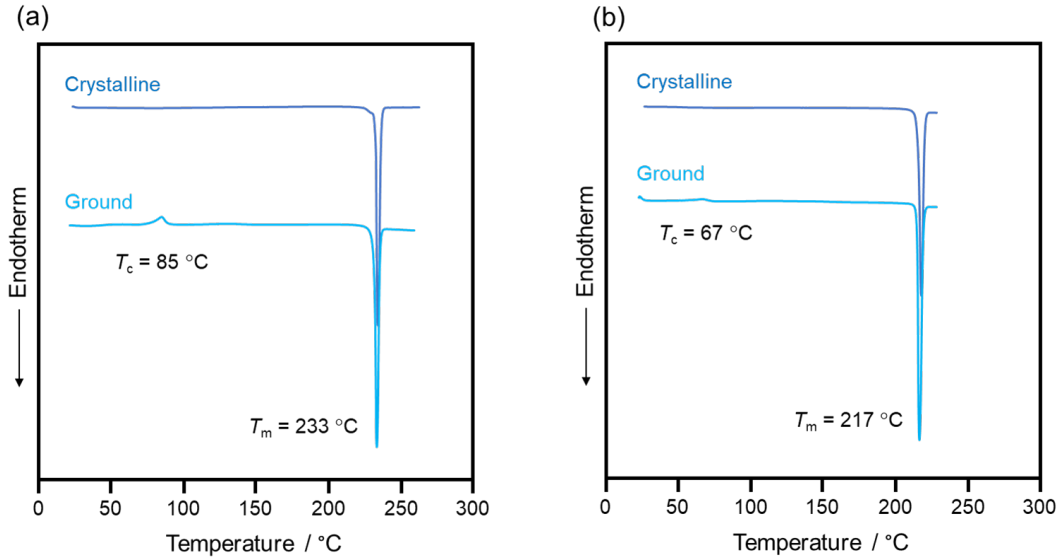


Fig. S1 DSC thermograms for crystalline and ground samples of (a) **1** and (b) **2**. T_c and T_m values are noted near the corresponding peaks.

2. Supplementary fluorescence spectra

*Fluorescence spectra for the stimuli-responsive luminescence of **2** and **2•HCl***

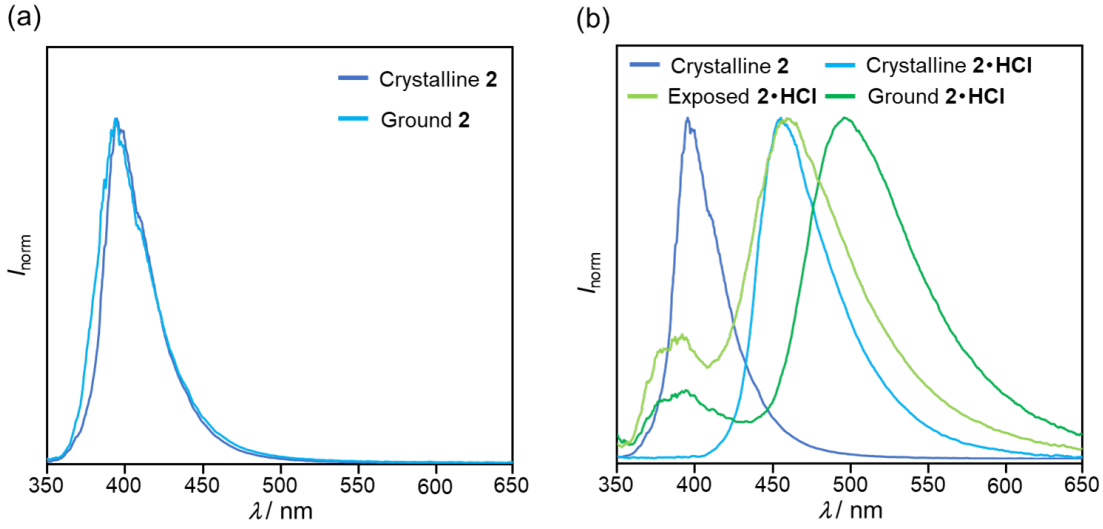


Fig. S2 Fluorescence spectra of (a) crystalline and ground **2** and (b) crystalline **2**, crystalline **2•HCl**, exposed **2•HCl**, and ground **2•HCl** under UV (310 nm) irradiation.

*Fluorescence spectra for crystalline **2**, crystalline **2•HCl**, and crushed **2•HCl***

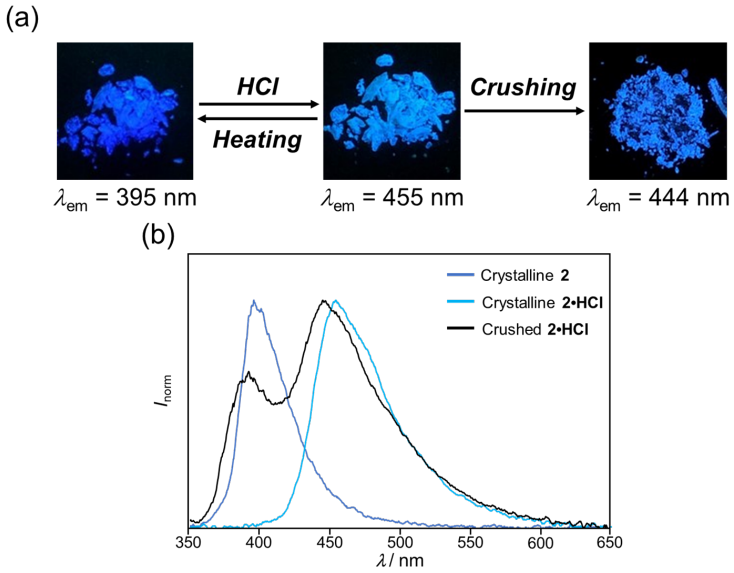


Fig. S3 (a) Photographs of **2**, **2•HCl**, and crushed **2•HCl** under UV (365 nm) irradiation. (b) Fluorescence spectra of **2**, **2•HCl**, and crushed **2•HCl** (λ_{ex} = 310 nm).

*Fluorescence spectra of ground **1•HCl** with **1** (0–2 equivalents)*

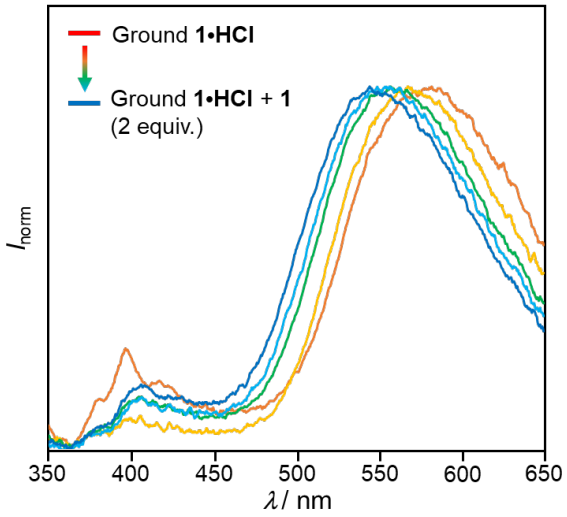


Fig. S4 Fluorescence spectra of ground **1•HCl** with **1** (0–2 equivalents) excited at 310 nm.

3. Powder X-ray diffraction (PXRD) patterns

*PXRD patterns of **2** and **2•HCl***

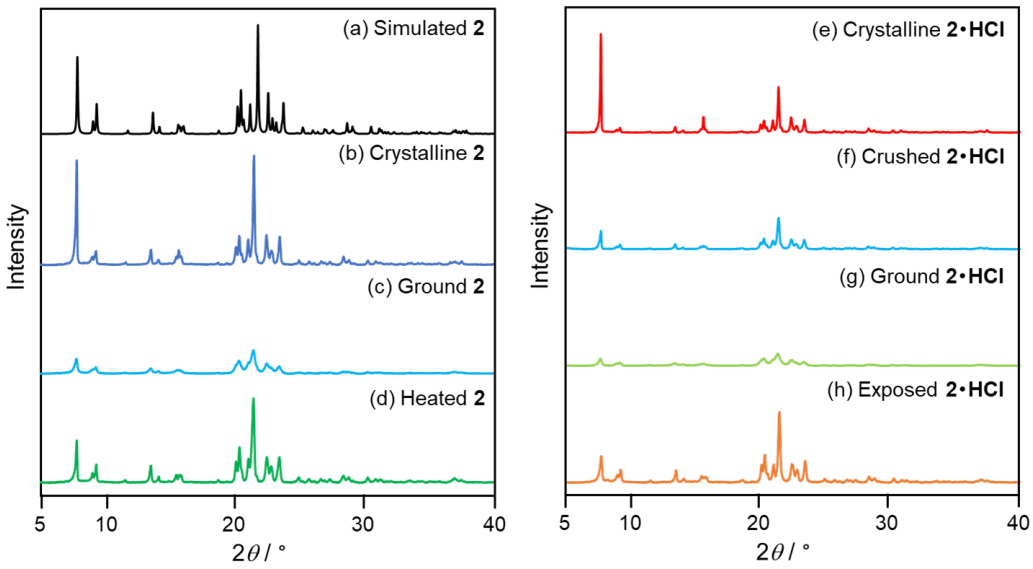


Fig. S5 (a) Simulated PXRD patterns of **2** calculated from the single-crystal X-ray diffraction structures prepared from $CHCl_3$/hexane. Experimental PXRD patterns for (b) crystalline, (c) ground, and (d) heated samples of **2** and (e) crystalline, (f) crushed, (g) ground, and (h) exposed to ethyl acetate samples of **2•HCl**.

*PXRD patterns of **1•HCl***

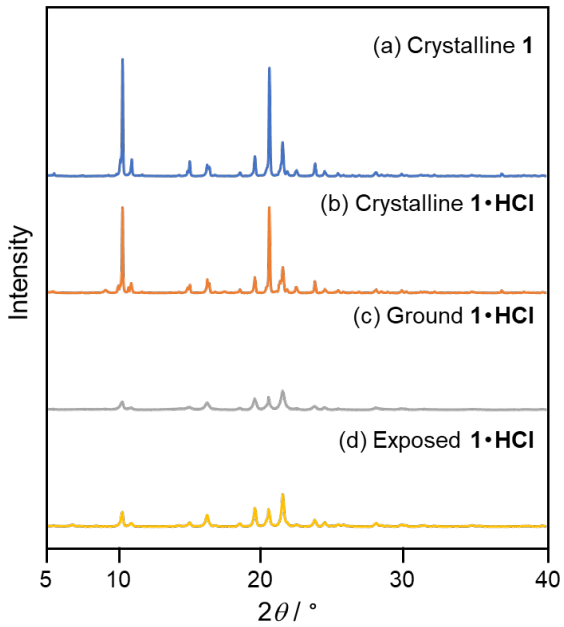


Fig. S6 PXRD patterns of (a) crystalline **1**, (b) crystalline **1•HCl**, (c) ground **1•HCl**, and (d) exposed **1•HCl**.

4. Theoretical calculations

Experimental absorption maxima and the results of DFT and TD-DFT calculations at the CAM-B3LYP/6-31G(d) level of theory are shown in Table S1. The HOMO and LUMO of **1**, **1•H**$^+$, **2**, and **2•H**$^+$ are shown in Fig. S7.

Table S1 Experimental absorption maxima and calculated absorption properties.

Compd.	Absorption in $CHCl_3$ λ_{abs} (nm)	Calcd absorption λ_{abs} (nm)	Transition from HOMO to LUMO	Oscillator strength	HOMO (eV)	LUMO (eV)	Dipole moment (D)
1	333	296.02	0.589	0.3874	–6.66	–0.16	4.64
1•H$^+$	428	432.04	0.696	0.7495	–9.39	–4.83	13.83
2	318	273.77	0.673	0.4344	–6.77	0.07	5.32
2•H$^+$	396	414.89	0.694	0.5817	–9.50	–4.73	13.68

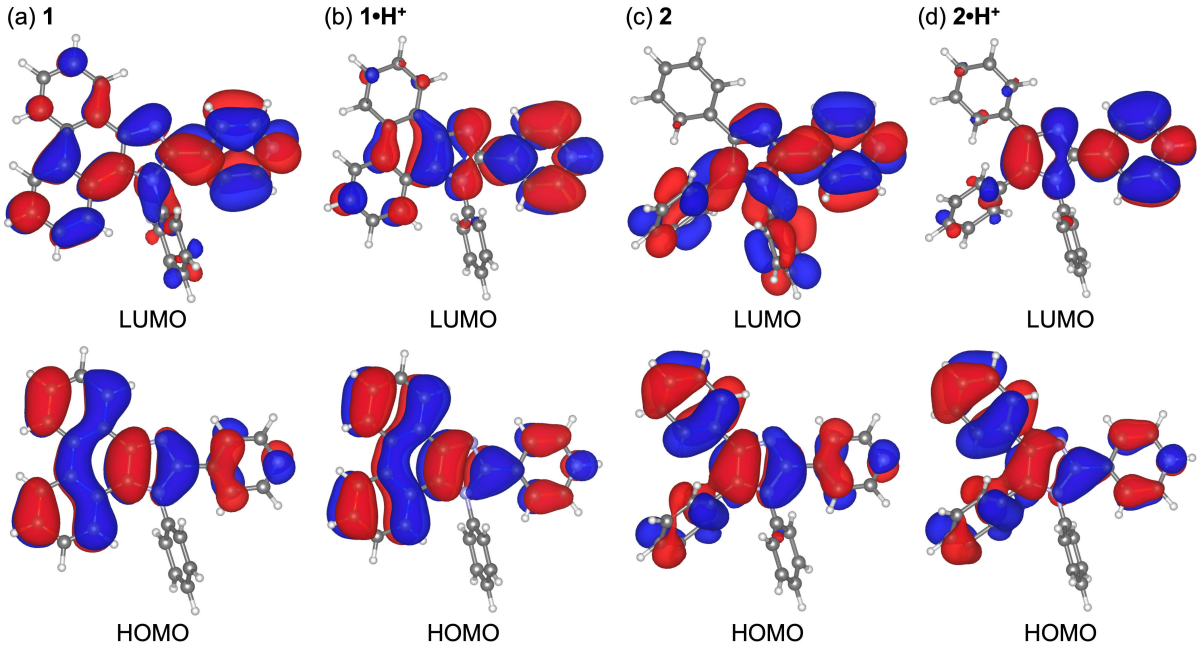


Fig. S7 HOMO and LUMO of **1** (a), **1•H**$^+$ (b), **2** (c), and **2•H**$^+$ (c) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[1]

5. Supplementary absorption and fluorescence spectra

*Absorption and fluorescence spectra of **2** and **2•HCl** in chloroform solution*

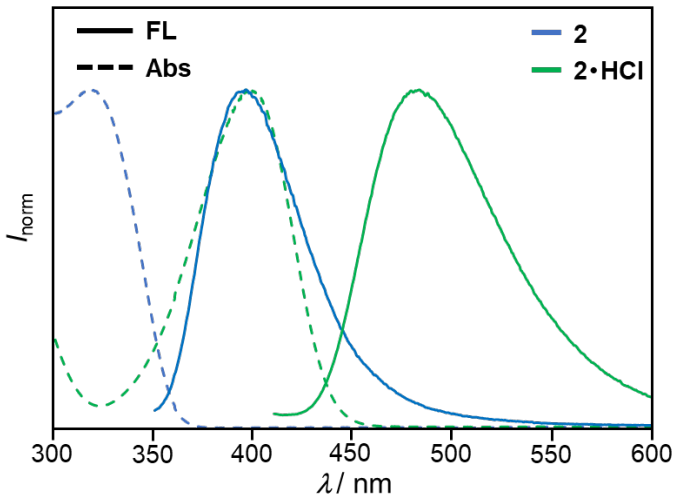


Fig. S8 Absorption (dotted line) and fluorescence (solid line) spectra of **2** and **2•HCl** in chloroform solution. Excitation wavelengths are 319 nm and 397 nm for **2** and **2•HCl**, respectively.

*Fluorescence spectra of **1** and **1•HCl** (after exposing to HCl vapor for 30 min) in chloroform*

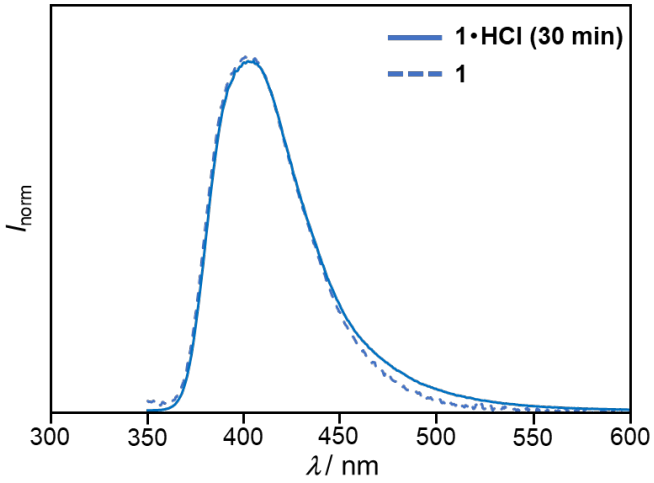


Fig. S9 Fluorescence spectra of **1** and **1•HCl** after exposing to HCl vapor for 30min. Excitation wavelengths are 331 nm and 333 nm for **1** and **1•HCl**, respectively.

Absorption spectra for solid-state samples

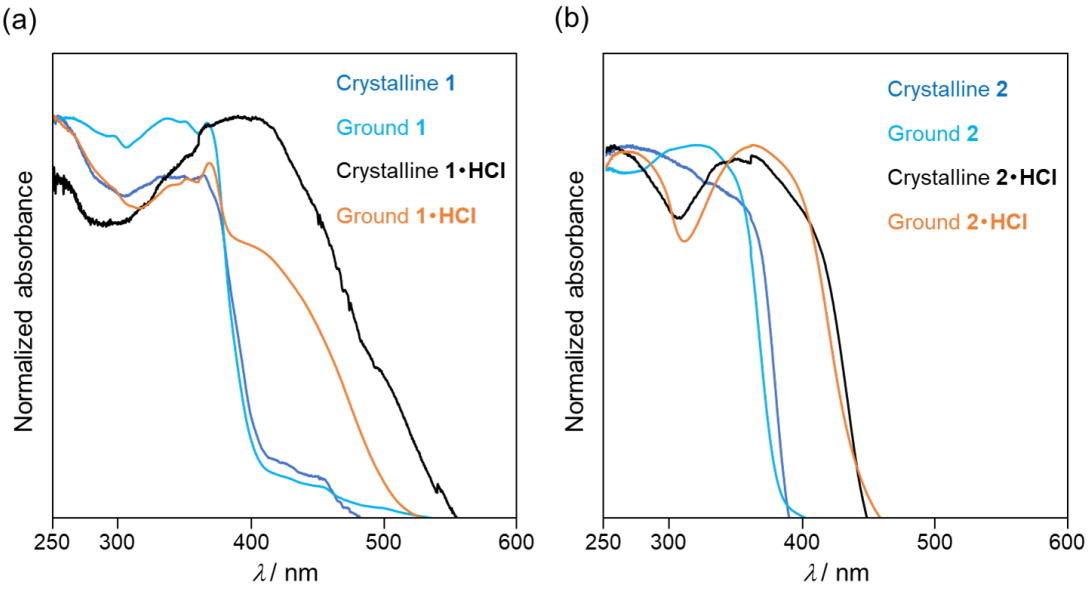


Fig. S10 Absorption spectra of crystalline and ground samples of (a) **1** and **1•HCl** and (b) **2** and **2•HCl**.

6. Supplementary excitation spectra

*Absorption and excitation spectra of **1**, **1•HCl**, **2**, and **2•HCl** in chloroform solution*

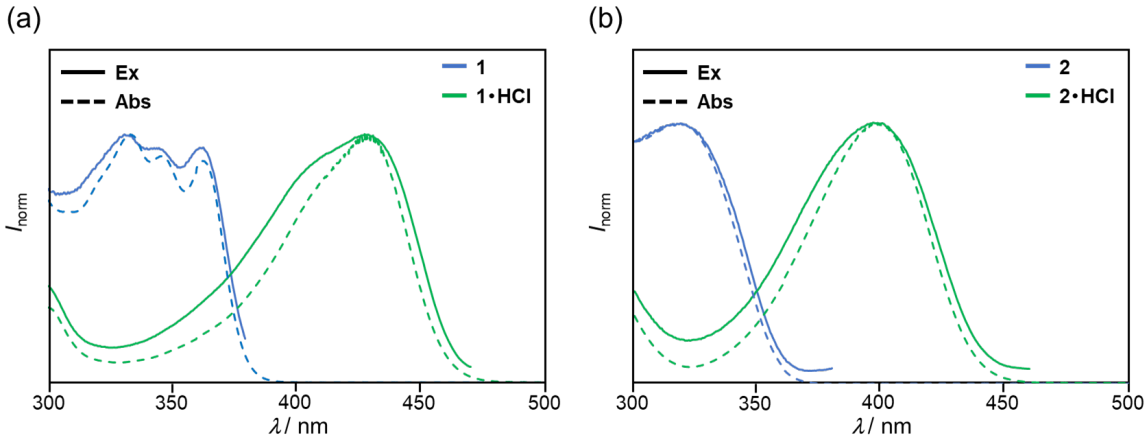


Fig. S11 Absorption (dotted line) and fluorescence (solid line) spectra of (a) **1** and **1•HCl** and (b) **2** and **2•HCl**.

7. Fluorescence microscopy

Fluorescence decay profiles

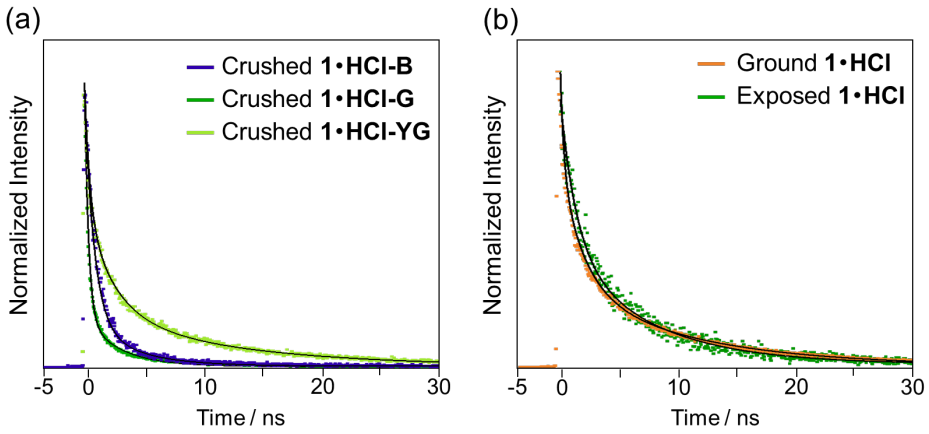


Fig. S12 Fluorescence decay profiles recorded by spatially resolved fluorescence microscopy (λ_{ex} = 405 nm). (a) Crushed **1•HCl-B**, **1•HCl-G**, and **1•HCl-YG**. (b) Ground and exposed **1•HCl**. The black lines indicate multi-exponential curves fitted to the time profiles.

Fluorescence spectra recorded by fluorescence microscopy

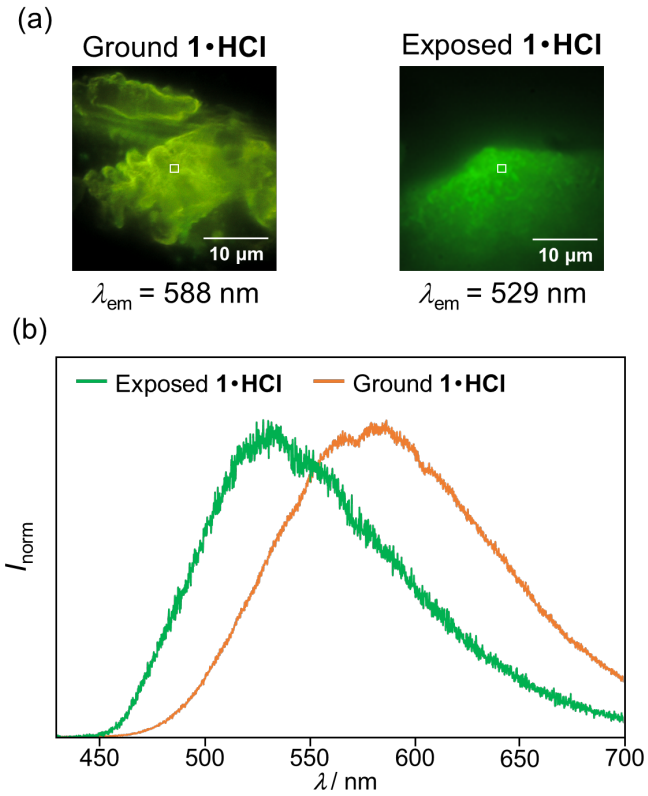
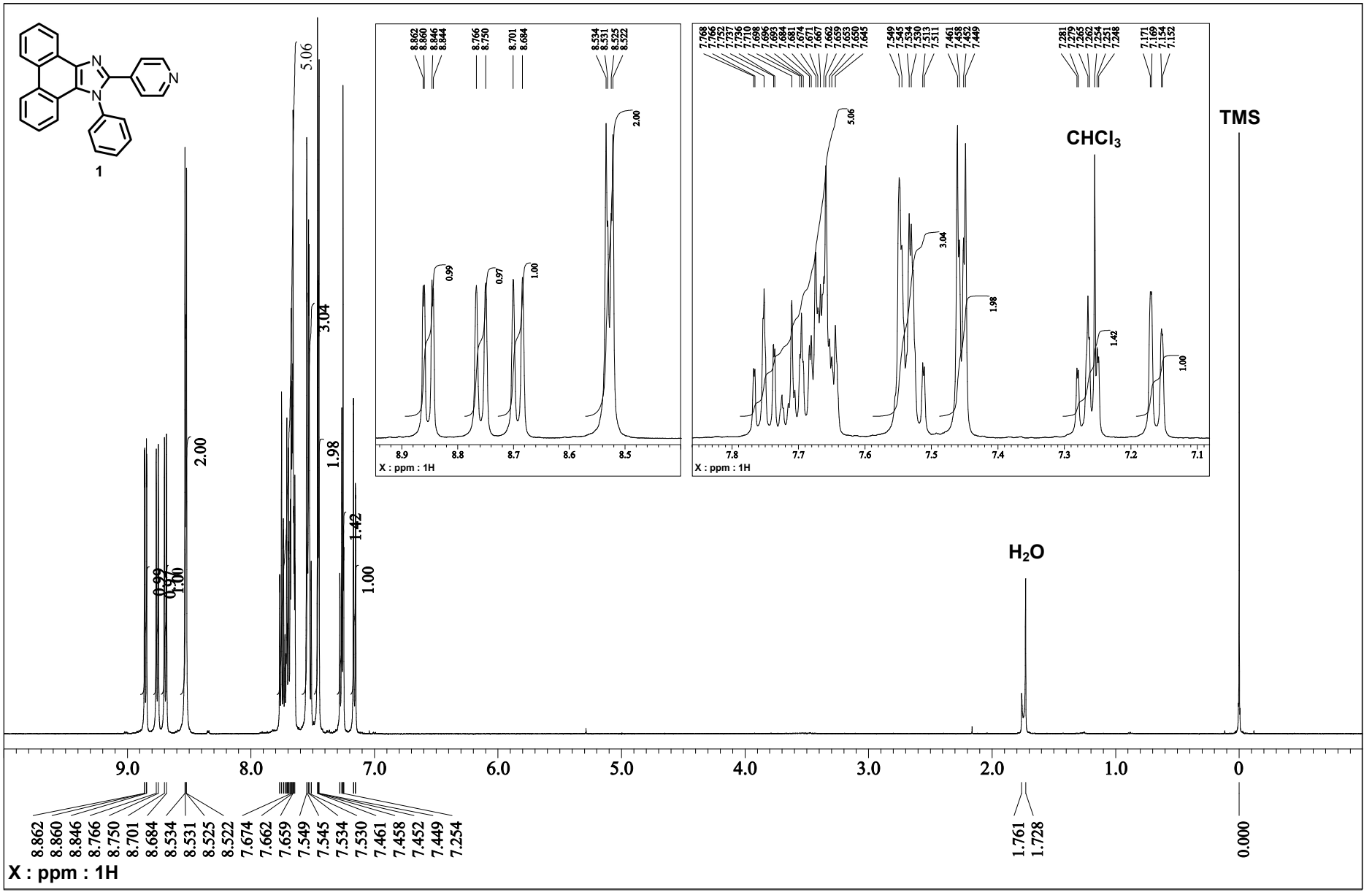


Fig. S13 (a) Photographs and (b) fluorescence spectra of ground and exposed **1•HCl** recorded by fluorescence microscopy (λ_{ex} = 405 nm). The square marks indicate the measured locations of fluorescence spectra and fluorescence decay profiles.

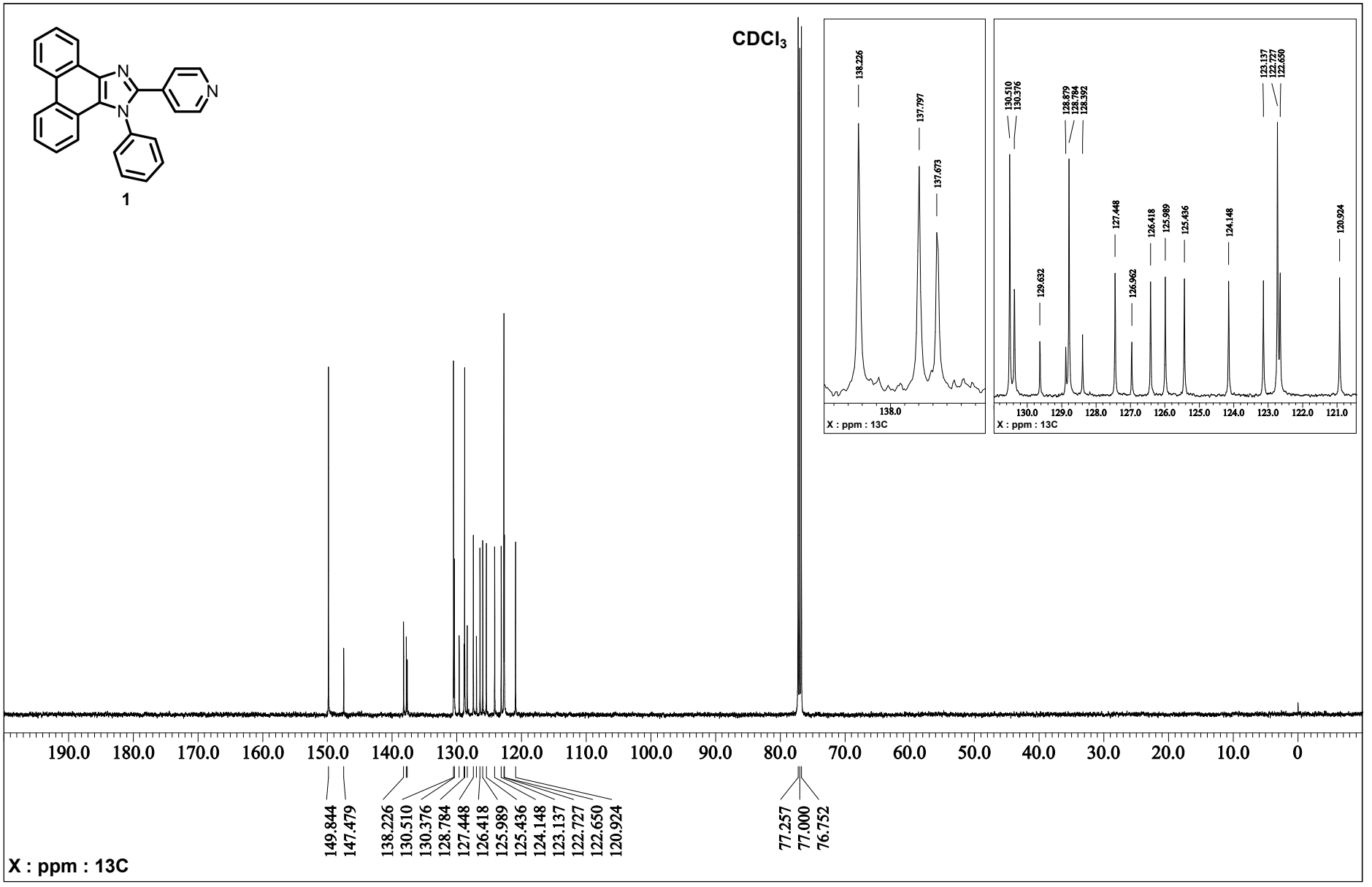
Reference

1) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.

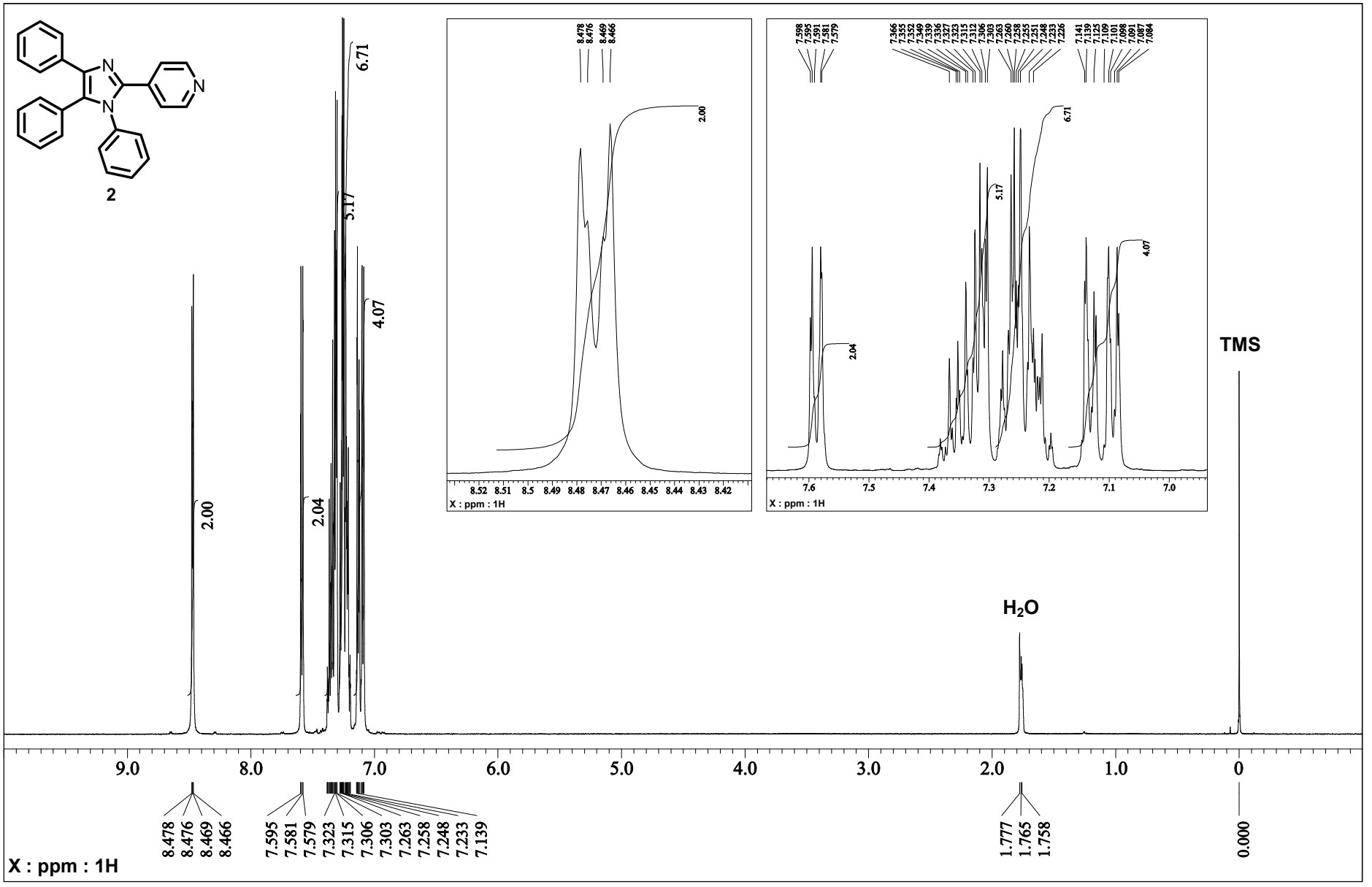
^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$, rt)



^{13}C NMR spectrum of **1** (126 MHz, $CDCl_3$, rt)



^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$, rt)



^{13}C NMR spectrum of **2** (126 MHz, $CDCl_3$, rt)