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Mechanochromic Luminescence from Crystals Consisting of Intermolecular Hydrogen-Bonded Sheets

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Abstract: Introduction of functional groups that can form intermolecular hydrogen bonds into highly-emissive luminophores is a promising way to induce mechanochromic luminescence. Herein, we report that a 9,10-bis(phenylethynyl)anthracene derivative featuring two amide groups forms green-emissive crystals based on two-dimensional hydrogen-bonded molecular sheets. Mechanical grinding changed the emission from green to yellow, owing to a transition from a crystalline to an amorphous phase. Infrared spectroscopy revealed that mechanical stimuli disrupted the linear hydrogen-bonding formation. A thermal treatment recovered the original green photoluminescence.

In the last decade, many compounds capable of changing their photoluminescence properties in response to mechanical stimuli have been reported.^[1–6] Such mechanoresponsive luminescent organic^[7–44] or organometallic^[45–57] compounds are regarded as useful for developing mechano-sensors to evaluate and/or visualize small forces. The use of molecular structures that show aggregation-induced emission (AIE)^[58–60] is one reliable way to achieve mechanoresponsive luminescence.^[2–5,16,32,59] Because AIE-active luminophores tend to form loosely-packed assemblies, mechanical stimuli induces closed-packing and/or conformational changes, which alter their photoluminescence properties. Another promising approach is the design of molecular structures in which different types of intermolecular interactions can compete against each other.^[2,7–9,13–14,21–24,27,31,37,39–44] Adopting this strategy, molecules can form several thermodynamically (meta)stable assembled states and mechanical stimuli can induce interconversions among these states. In particular, competition between hydrogen-bonding and π – π stacking is effectively achieved by introducing amide groups directly into luminophores.^[7–8,13,21,23,37,39–42] This effectiveness is attributed to the fact that the length between amide groups forming hydrogen bonds is generally longer than the distance between aromatic groups forming π – π stacks. However, mechanoresponsive luminescent compounds in which several amide groups are directly introduced into one π -extended aromatic moiety have rarely been reported. This lack of previous reports is likely because the combination of π – π stacking and multiple hydrogen bonds decreases the solubility of these molecules unless large and flexible substituents are attached.^[8,14,21,23,39–42]

Here, we demonstrate that the molecular design strategy described above is significantly effective using a simple

anthracene derivative. 9,10-Bis(phenylethynyl)anthracene derivative **1** (Figure 1a) forms a two-dimensional (2D) molecular sheet constructed from intermolecular hydrogen bonds between the amide groups in the green-emissive crystals (G-form). Mechanical grinding to the G-form disrupts a part of the linear hydrogen-bonding network. After grinding, the luminophores form excimer-like species and the emission color changes from green to yellow (Figure 1b). Furthermore, the resultant yellow-emissive amorphous (Y-form) can be converted to the initial green-emissive crystalline state after a thermal treatment. To our knowledge, the mechanoresponsive property exhibited by **1** is the first example of mechanochromic luminescence from two-dimensionally hydrogen-bonded molecular sheets.

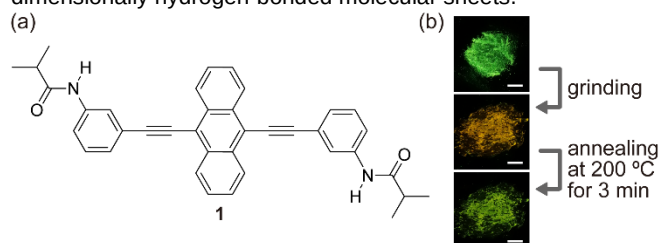


Figure 1. (a) Molecular structure of 9,10-bis(phenylethynyl)anthracene derivative **1**. (b) Mechanochromic luminescence exhibited by compound **1**. Photographs were taken under excitation at 365 nm. Scale bar: 3 mm.

Compound **1** was synthesized from 9,10-dibromoanthracene and *N*-(3-ethynylphenyl)isobutyramide through a Sonogashira coupling and exhibits green photoluminescence under excitation at 365 nm. The ester analogue compound **2** was also prepared (see the Supporting Information). Compound **1** is poorly soluble in toluene, acetonitrile, ethyl acetate, chloroform, THF, methanol, and diethyl ether but dissolves in DMF and DMSO on heating. Fortunately, crystals suitable for single crystal X-ray structure analysis were obtained from recrystallization from a mixture of DMF and chloroform (1:1, v/v) as the solvent. Anthracene derivative **1** crystallized with the space group of $P2_1/n$. Half of the molecule was crystallographically independent because the inversion center corresponds to the center of anthracene ring. The planes of the phenylene rings at both ends in the molecule were tilted 66.98° from the plane of the anthracene ring (Figure 2a). The distance between the N and O atoms of the adjacent molecule was 2.752 Å, and the corresponding N–H...O angle was 154.98° ; hence, the amide groups interacted with each other through a moderate hydrogen bond.^[61] The N–H...O hydrogen bonds extended one-dimensionally, forming a $\cdots[\text{O}=\text{C}-\text{N}-\text{H}\cdots\text{O}=\text{C}-\text{N}-\text{H}]\cdots$ hydrogen-bonding chain. All molecules involved in the hydrogen-bonding chain are interdigitated at both terminals of the molecule, assembled as 2D sheet parallel to the (2 0 1) plane (Figure 2b). The low solubility of **1** in common organic solvents is attributed to the interdigitated molecular assemblies mediated by the intermolecular hydrogen bonds in the 2D molecular sheet. Between the 2D sheet structures, anthracene rings are arranged in parallel with an interplanar spacing of 3.421 Å. One of the three

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aromatic rings in anthracene stacks continuously along the $[2\ 0\ 1]$ direction (Figure 2c).

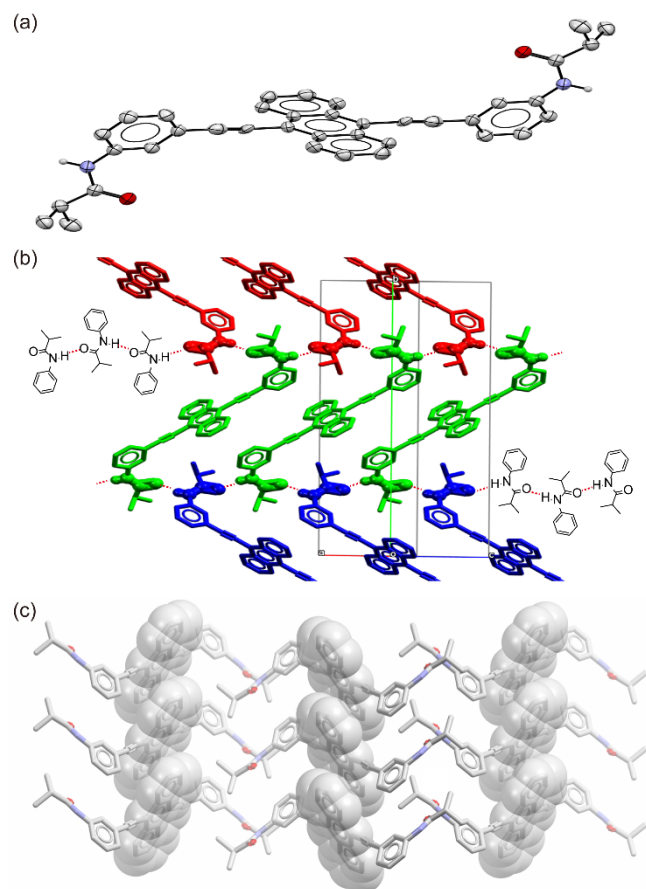


Figure 2. Crystal structure of **1**. Hydrogen atoms are omitted for clarity except for those involved hydrogen bonds. (a) Ortep drawing of molecular structure in a single crystal **1**. (b) Interdigitated 2D molecular assembly parallel to the $(2\ 0\ 1)$ plane, formed by linear hydrogen bonds between amide groups. Schematic diagrams of linear hydrogen bonding are also shown. (c) Three-dimensional stacked structure viewed along the direction of linear hydrogen bonds. Slipped π - π stack between anthracene rings illustrated by space filling model and other atoms shown as a stick model.

X-ray diffraction (XRD) measurements were performed to clarify the change in molecular assembled structure by mechanical grinding. The crystalline G-form has many sharp peaks reflecting its crystalline nature (Figure 3a). The XRD diffractogram is similar to that calculated from single crystal analysis data (Figure S2). Almost all peaks disappeared in the diffraction pattern recorded for the yellow-emissive Y-form (Figure 3b), indicating that mechanical grinding induced a transition from the crystal to an amorphous phase. As the hydrogen-bonded molecular sheet shown in Figure 2b is a highly-ordered structure, several weak peaks remained in the XRD pattern (Figure 3b). After thermal treatment of the Y-form at 200 °C for 3 min, diffraction peaks corresponding to the G-form reappeared (Figure 3c). Thus, the annealing process converted the Y-form to the G-form, which showed green emission.

Differential scanning calorimetry (DSC) measurements were performed to obtain more insight into the mechanical stimuli-induced transition. The heating curve of the G-form had no peaks

from room temperature (r.t.) to 240 °C (Figure S3a). Conversely, one peak was observed at 112.9 °C in the DSC curve recorded for the Y-form on heating (Figure S3b). This peak is attributed to the transition from the amorphous to crystalline phase. Because this peak is exothermic, the Y-form is a thermodynamically metastable state. A large exothermic peak corresponding to the decomposition of compound **1** in the G-form appears around 350 °C on further heating DSC trace (Figure S4a), which was also confirmed by polarized optical microscopic observations. Thermogravimetric analyses (TGA) revealed that the weight of the G-form gradually decreased above the decomposition temperature (Figure S4b).

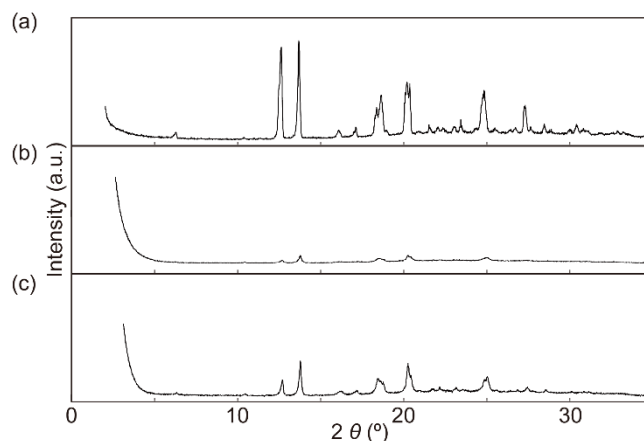


Figure 3. XRD diffractograms of **1** (a) in the G-form, (b) in the Y-form, and (c) after annealing at 200 °C for 3 min for the Y-form. All diffractograms were obtained at r.t..

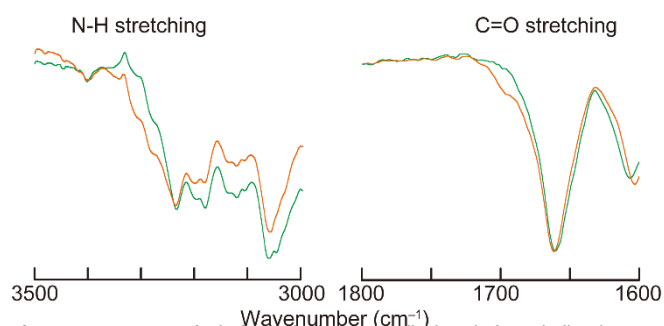


Figure 4. IR spectra of **1** before grinding (green line) and after grinding (orange line). Spectra were recorded at room temperature.

Infrared (IR) spectroscopy measurements clarified the effect of the grinding on the hydrogen bonds between amide groups of **1**. The IR spectrum for **1** in the G-form had peaks corresponding to C=O and N-H stretching at 1660 and 3235 cm⁻¹, respectively (Figure 4, green lines). This observation confirmed that amide groups were involved in the formation of hydrogen bonds and no free amide groups were present, which is consistent with the single crystal X-ray structure analysis (Figure 2b). After mechanical grinding, no peaks indicative of free amide groups appeared in the IR spectrum (Figure 4, orange line). This result suggests that hydrogen bonds were not cleaved by mechanical stimuli. However, closer inspection revealed that both C=O and N-H stretching bands extended to higher wavenumbers.^{[7-8,13-}

^{14,42,43]} Changes in the peak shapes indicated the presence of weakly hydrogen-bonded amide groups after grinding. Therefore, mechanical stimuli disrupted the linear hydrogen-bonding formation in the crystalline G-form (Figure 2b) to some degree.

Spectroscopic measurements of the DMF solution of compound **1** ($c = 1.0 \times 10^{-5}$ M) were conducted to obtain the fundamental photophysical properties of individual molecules. As shown in Figure 5a, the absorption band between 400 and 500 nm had two peaks at 443 and 468 nm with molar absorption coefficients of 3.7×10^4 L mol⁻¹ cm⁻¹ and 4.1×10^4 L mol⁻¹ cm⁻¹, respectively. Vibronic structure was observed in the emission spectrum of **1** in DMF with two peaks at 482 and 511 nm and a shoulder at 550 nm (Fig. 5b). These spectral features are typical for 9,10-bis(phenylethynyl)anthracene derivatives.^[14,26,62-65] Therefore, compound **1** molecularly disperses in DMF solution. The photoluminescent quantum efficiency (PLQY) of the DMF solution was 0.96.

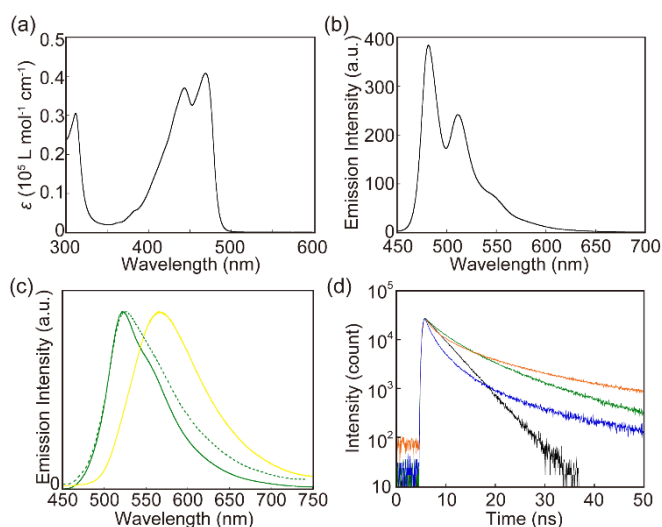


Figure 5. Photophysical properties of compound **1** in solution and solid states. (a) Absorption and (b) photoluminescence spectra of **1** in DMF ($c = 1.0 \times 10^{-5}$ M). (c) Photoluminescence spectra of the G-form (green solid line), Y-form (yellow solid line), and annealed Y-form (green dotted line). (d) Emission decay profiles recorded for the DMF solution of **1** (black), G-form (green), Y-form (orange), annealed Y-form (blue). All spectra and decay profiles were obtained at r.t.. Emission spectra were recorded with excitation at 400 nm. The decay profiles were monitored with excitation at 405 nm.

Next, we examined mechanochromic luminescence behavior of **1**. The G-form displayed an emission peak at 521 nm and a shoulder around 560 nm (Figure 5c, green solid line). The shoulder would be ascribed to vibronic structure of the luminophore. The mechanical grinding induced a phase transition from the G-form to the Y-form resulting in a redshift of the emission spectrum. The emission spectrum of the Y-form had a peak at 567 nm (Figure 5c, yellow solid line). The broad and structureless spectral shape is attributed to the formation of excimer-like emission species between the luminophores. This is supported by the fact that an ester analogue compound **2** displays a broad and structureless excimer emission band with a peak at 550 nm in chloroform under a high concentration condition ($c = 1.0 \times 10^{-2}$ M) (Figure S5). The PLQYs of the G-form and Y-form were 0.17 and 0.21, respectively. After thermal treatment to the Y-form at 200 °C for 3 min, the emission peak blue-shifted from

567 to 525 nm (Figure 5c, green dotted line), indicating that green emission recovered although the emission intensity in the longer wavelength region was slightly greater than that of the G-form. The shoulder observed in the emission spectrum of the initial G-form disappears due to the incomplete recovery. It is noteworthy that the ester analogue **2** also exhibits mechanochromic luminescence, indicating that amide groups are not essential to induce the mechanoresponsiveness for the molecular skeleton (Figure S6).

Table 1. Emission lifetimes of **1** in solution and solid states.

	τ (ns)	χ^2
1 in DMF ^{a)}	3.1	1.02
1 in the G-form ^{b)}	1.8, 4.7, 12	1.01
1 in the Y-form ^{c)}	1.7, 5.7, 20	1.05
1 in the annealed Y-form ^{b)}	1.3, 3.7, 13	1.06

^{a)} Monitored at 480 nm. ^{b)} Monitored at 520 nm. ^{c)} Monitored at 560 nm.

Emission lifetime measurements were performed to gain more insight into the mechanochromic luminescence shown by **1**. The DMF solution of **1** had an emission decay profile that was well-fitted by a single exponential decay function (Figure 5d, black line) and the calculated lifetime was 3.1 ns, which is indicative of monomer emission. The G-form, Y-form, and annealed Y-form gave decay curves that were fitted with triexponential decay functions. The calculated lifetimes are listed in Table 1. A relatively long lifetime of 12 ns and short lifetimes of 1.8 and 4.7 ns were measured for the initial G-form. As shown in Figure 2b, no π - π stacking of the emission cores occurs in the intermolecular hydrogen bond-directed molecular sheet. Therefore, the former emission species is attributed to the small overlap of luminophores between the molecular sheets (Figure 2c). Compared with the G-form, the Y-form has a longer lifetime of 20 ns, which corresponds to emission of excimer-like species that give yellow photoluminescence. Notably, the luminophores are not fully overlapped in the same way as conventional excimers because the excimers of 9,10-bis(phenylethynyl)anthracene derivatives normally give the emission band at longer wavelengths.^[14,26] We assumed that strong intermolecular hydrogen bonding prevented the luminophores from forming ideal excimers even when heavily ground. Indeed, the emission band of ground **2** was observed in slightly longer wavelength region compared to that of the Y-form (Figure S6). After the thermal treatment for the Y-form, long emission lifetimes were not observed, suggesting that excimer-like emission species were almost completely absent.

In conclusion, we demonstrated that introducing several amide groups into a flat luminophore is a promising way to achieve mechanoresponsive luminescence using a simple anthracene derivative. The approach allowed us to access mechanochromic luminescence from two-dimensionally hydrogen-bonded molecular sheet. The 9,10-bis(phenylethynyl)anthracene derivative **1** having two amide groups forms a two-dimensional molecular sheet constructed by intermolecular hydrogen bonds in the green-emissive crystals. On grinding the sample, a phase transition from a crystal to an amorphous phase occurs and the emission color changes to yellow, owing to the formation of excimer-like emission species.

Additionally, part of the linear hydrogen-bonding structure is disturbed, as confirmed by IR spectroscopy. Furthermore, thermal treatment recovers the initial crystalline structure and green photoluminescence. Because luminophores having several amide groups have not been well explored from the viewpoint of mechanochromic luminescence, the investigation of other luminophores with multiple hydrogen-bonding groups is ongoing in our group.

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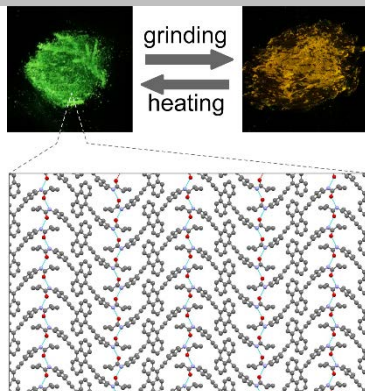
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COMMUNICATION

A 9,10-bis(phenylethynyl)anthracene derivative featuring two amide groups forms green-emissive crystals based on two-dimensional intermolecular hydrogen-bonded sheets. When mechanically ground, linear hydrogen bonding was partially disturbed and the resultant excimer-like species showed yellow emission. Thermal treatment recovered the initial crystalline state.



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