A Water-Soluble Mechanochromic Luminescent Pyrene Derivative Exhibiting Recovery of the Initial Photoluminescence Color in a High-Humidity Environment

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Switching of the luminescence properties of molecular materials in response to mechanical stimulation is of fundamental interest and also has a range of potential applications. Herein, a water-soluble mechanochromic luminescent pyrene derivative having two hydrophilic dendrons is reported. This pyrene derivative is the first example of a mechanochromic luminescent organic compound that responds to relative humidity. Mechanical stimulation (grinding) of this pyrene derivative in the solid state results in a change of the photoluminescence from yellow to green. Subsequent exposure to water vapor induces recovery of the initial yellow photoluminescence. The color change is reversible through at least ten cycles. It is also demonstrated that this compound can be applied as a mechano-sensing material in frictional wear testing for grease, owing to its immiscibility in non-polar solvents and its non-crystalline behavior. Transmission electron microscope and atomic force microscope observations of samples prepared from dilute aqueous solutions of the pyrene derivative on suitable substrates, together with dynamic light scattering measurements for the compound in aqueous solution, indicate that this amphiphilic dumbbell-shaped molecule forms micelles in water.

1. Introduction

Organic molecular materials that exhibit a change in the color of their luminescence in response to external stimulation have attracted much interest because of their potential applications, for example, in memory, sensors, informational displays, and bioimaging.[1–4] Switching of the assembled structures of luminescent groups is considered one of the most promising ways to obtain such luminescent materials.[3,4] Over the last decade, various types of organic compounds,[5] organometallic compounds[6] and dye-doped polymers[7] have been reported to show changes in photoluminescence color in response to mechanical stimulation. This phenomenon is referred to as mechano(piezo)chromic luminescence or mechanofluorochromism. In the case of some mechanochromic luminescent compounds, the initial photoluminescence color can be recovered through subsequent exposure to vapor of organic solvents such as acetone, methylene chloride and tetrahydrofuran.[5e,g,i,o,p,q,6b,d] However, no organic and/or organometallic mechanochromic luminescent material that recovers its initial photoluminescence color upon exposure to water vapor has been prepared. Moreover, to our knowledge, no mechanochromic luminescent compound that is soluble in water has been reported, except for one organic compound.[5q] Such a material would potentially be useful for biocompatible luminescent mechanosensors and humidity sensors. Here we report water-soluble mechanochromic luminescent pyrene derivative **1** (**Figure 1**), which shows a photoluminescence color change from yellow to green in response to mechanical grinding and recovers the initial yellow photoluminescence upon subsequent exposure to water vapor (**Figure 2**). Though our group and other groups have prepared crystalline or liquid-crystalline pyrene derivatives with mechanochromic luminescent properties, the reported pyrene derivatives do not exhibit any change in photoluminescence color in response to changes in relative humidity.[5a,c,k,l,n,q]

2. Results and Discussion

2.1. Molecular Design and Changes in the Photoluminescence Color

Compound **1** has a pyrene group as the luminescent core and two dendritic groups[8] that are attached to the luminescent core through amide groups. Introduction of non-covalent intermolecular interactions such as hydrogen bonds is known to be an effective way to align luminophores for the development of sophisticated photofunctional materials.[9] To increase

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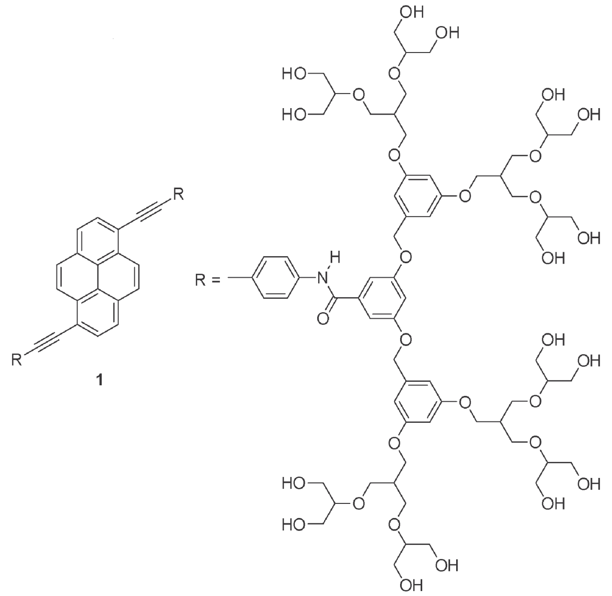

Figure 1. Molecular structure of amphiphilic pyrene derivative **1**.

Figure 3. Photoluminescence image of dilute methanol (left) and water (right) solutions of **1**. The images were taken under UV irradiation (365 nm) at room temperature.

water-solubility, 32 hydroxyl groups were incorporated into the dendrons at peripheral positions. We expected that compound **1** would form molecular assemblies in water, because of its amphiphilic character. It is well known that amphiphiles consisting of rigid aromatic moieties and hydrophilic flexible groups self-assemble into various types of supramolecular structures, including spherical micelles, cylindrical micelles, hollow vesicles and planar membranes.[10]

The dumbbell-shaped compound **1** was obtained as a cottony yellow solid (Y-form) after purification by gel permeation chromatography (GPC) and lyophilization of the aqueous solution. Under UV irradiation (365 nm), yellow photoluminescence was observed for **1** in the Y-form (Figure 2, left). Mechanical grinding caused a luminescence color change from yellow to green (Figure 2, left → middle). This is typical mechanochromic luminescent behavior. However, unexpectedly, we also found that the initial yellow photoluminescence was recovered when the green luminescence-emitting state (G-form) was exposed to water vapor (Figure 2, middle → right). No previously reported luminescent organic and/or organometallic material shows such reversible changes in photoluminescence color in response to mechanical stimulation and exposure to water vapor.

We next examined the solubility of the amphiphilic pyrene derivative. Compound **1** is soluble in polar solvents such as methanol, ethanol, *N*,*N*-dimethylformamide, dimethylsulfoxide, pyridine and water at room temperature, but not in hexane, ethyl acetate, methylene chloride, chloroform, toluene, tetrahydrofuran or acetonitrile at room temperature. We found that methanol, ethanol, *N*,*N*-dimethylformamide, dimethylsulfoxide and pyridine solutions of **1** exhibited blue photoluminescence under UV irradiation (365 nm), whereas yellow photoluminescence was observed for an aqueous solution of **1** (**Figure 3**), indicating that aggregation of **1** occurs in water.

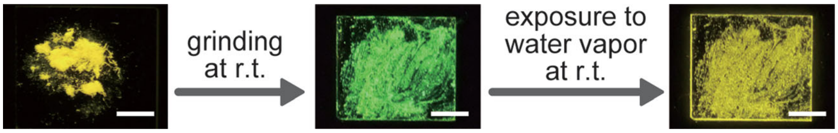

Figure 2. Change in the luminescence color of compound **1** in the solid state. The photoluminescence images were taken on quartz substrates under UV irradiation at 365 nm. Scale bar: 5 mm.

2.2. Photophysical Properties

Spectroscopic measurements were performed to obtain further insight into the changes in the photoluminescence color of **1** in the solid state. Absorption and emission spectra of **1** in methanol (1.0×10^{-5} M) (**Figure 4**a,b, blue solid lines) have well-resolved vibronic structures, suggesting that compound **1** is monomeric in methanol at the concentration of 1.0×10^{-5} M. In water (1.0×10^{-5} M), the absorption band between 350 and 500 nm is broadened compared to that of **1** in methanol (Figure 4a), indicating that ground-state electronic interactions between the luminescent groups occur in water. As shown in Figure 4b, the emission spectral features of **1** in methanol and water are clearly different. The emission spectrum of **1** in water is significantly red-shifted and broadened (Figure 4b, orange solid line) in comparison with that of **1** in methanol (Figure 4b, blue solid line). The broad and structureless emission band at λ_{max} = 548 nm can be ascribed to excimer formation[11] of the pyrene moieties of **1**. Emission decay time measurements were consistent with excimer formation, i.e., compared to the emission lifetime for **1** in methanol solution (1.0 ns), a longer lifetime component of 63 ns was observed for compound **1** in water at room temperature. The

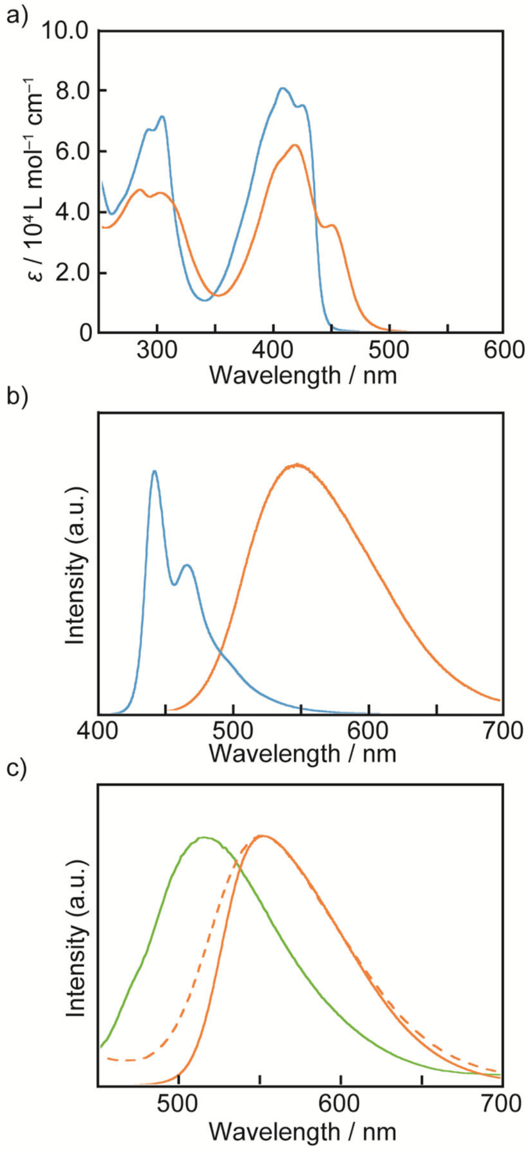

Figure 4. a) Absorption and b) emission spectra of compound **1** in methanol (1.0×10^{-5} M, blue solid line) and in water (1.0×10^{-5} M, orange solid line). c) Emission spectra of **1** in the Y-form (RH < 5%, orange solid line), **1** after mechanical grinding (G-form, RH < 5%, green solid line) and **1** exposed to water vapor after mechanical grinding (RH = 100%, orange dotted line). All absorption and emission spectra were obtained at room temperature. $\lambda_{ex} = 400$ nm.

quantum efficiencies of **1** in methanol and water are 0.74 and 0.57, respectively.

The emission spectra of **1** in the solid state were recorded using handmade optical cells in which the relative humidity (RH) was kept constant (Figures S1 and S2). The emission spectrum of **1** in the Y-form (RH < 5%) displays a broad and structureless band with an emission maximum at $\lambda = 551$ nm (Figure 4c, orange solid line). This spectral feature is similar to that of **1** in water (Figure 4b, orange solid line), indicating that excimer formation of the luminescent cores of **1** also occurs in the Y-form. After mechanical grinding, the emission band of **1** (RH < 5%) (Figure 4c, green solid line) is blue-shifted with respect to that of **1** in the Y-form. This spectral shift corresponds to the change in photoluminescence color from yellow to green (Y-form → G-form) (Figure 2, left → middle). The observed green emission ($\lambda_{max} = 515$ nm) can be ascribed to partial-overlap excimers.[12] Partial-overlap excimer formation has been observed in some mechanochromic luminescent materials, as well as in highly viscous media such as polymers and Langmuir–Blodgett films.[5j,12] Emission bands derived from partial-overlap excimers often appear between monomer emission bands and normal excimer emission bands. In addition, emission lifetimes for partial-overlap excimers are often shorter than those for normal excimers. Thus, the photophysical properties of **1** in the G-form are consistent with the formation of partial-overlap excimers. In the G-form, compound **1** contains a component with a lifetime (29 ns) shorter than that of the excimer of the luminescent core of **1** and longer than that observed for the methanol solution, in which compound **1** is monomeric. When compound **1** in the G-form was exposed to 100% RH, the emission band was red-shifted immediately (Figure 4c, green solid line → orange dotted line), which corresponds to the photoluminescence color change from green to yellow (Figure 2, middle → right). The maximum ($\lambda_{max} = 552$ nm) of the emission band after exposure to 100% RH (3 hours) is at the same position as that of compound **1** in the Y-form before grinding, though the emission spectral shape does not recover completely in the shorter-wavelength region. The incomplete recovery may be partially ascribed to the reabsorption in the initial Y-form.

Subsequent grinding of this sample under ambient conditions induced green photoluminescence under UV irradiation. This cycle between the two different photoluminescent colors can be repeated at least ten times (**Figure 5**). Therefore, the pyrene derivative **1** appears to be a good candidate for both mechano-sensors and humidity sensors. Though the quantum yields of pyrene derivative **1** in Y-form ($\Phi = 0.54$) and G-form ($\Phi = 0.38$) are lower than those observed for **1** in solution, these values are sufficient for practical mechano-sensors and humidity sensors.

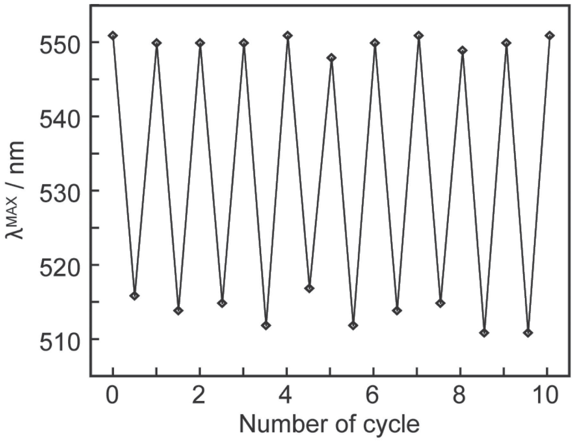

Figure 5. Changes in the photoluminescence color of **1** upon repeated cycles of grinding followed by exposure to high humidity (RH = 100%). $\lambda_{ex} = 400$ nm.

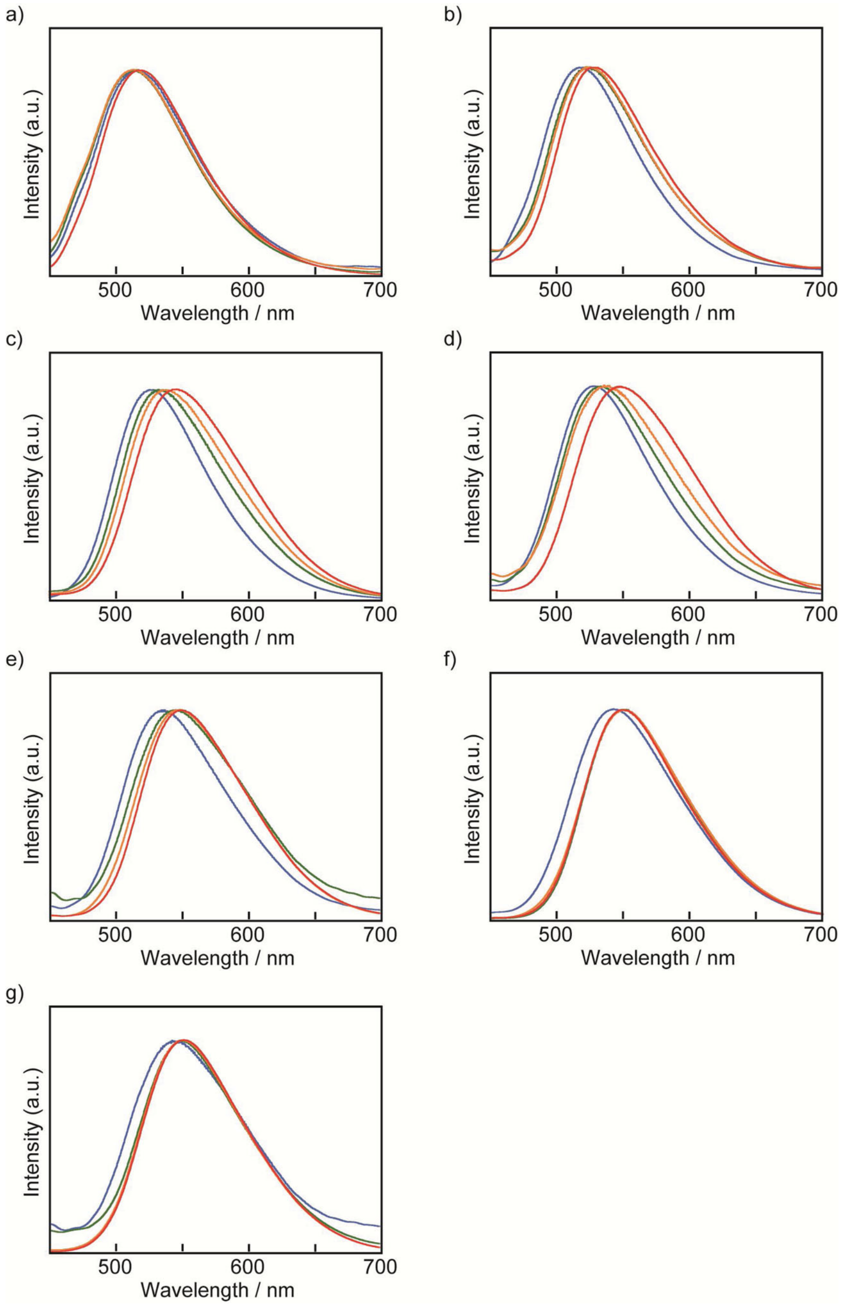

Figure 6. Time-dependent photoluminescence spectra of **1** in the solid state at 20 minutes (blue line), 3 hours (green line), 1 day (orange line), and 1 week (red line) after grinding; a) RH < 5%, b) RH = 20%, c) RH = 42%, d) RH = 58%, e) RH = 79%, f) RH = 95%, g) RH = 100%.

Time-dependent changes in the emission spectra of **1** at various RH values were also recorded (**Figure 6**). Compound **1** was ground on quartz substrates under ambient conditions and immediately transferred into handmade optical cells, as shown in Supporting Information Figure S1 and S2. When compound **1** was exposed to RH < 5%, no marked change in the emission band was observed for at least one week (Figure 6a). On the other hand, when compound **1** was exposed to RH > 79%, the emission color change from green to yellow within 3 hours (Figure 6e–g).

2.3. Molecular Assembled Structures

To clarify the nature of the molecular assemblies of **1** in water, transmission electron microscope (TEM) and atomic force microscope (AFM) images were obtained, and the hydrodynamic radius distribution was evaluated (**Figure 7**). The TEM images of samples prepared by coating a dilute aqueous solution of **1** onto a copper grid and staining with uranyl acetate (Figure 7a and Supporting Information Figure S3) displayed many micellar structures with diameter between 5 and 10 nm, indicating that compound **1** forms micelles in water. From dynamic light scattering (DLS) measurements (Figure 7b), the average hydrodynamic radius of the micelles of **1** in water was approximately 7 nm, which is consistent with the observed diameter of micelles in the TEM images and with the molecular length of **1**. AFM analysis of samples prepared by drop-casting a dilute aqueous solution of **1** onto a glass substrate (Figure 7c and Supporting Information Figure S4) was also consistent with the formation of micellar structures in water, exhibiting micelles with a height of 5–8 nm. Because compound **1** in the Y-form was obtained through freeze-drying of an aqueous solution of **1**, the micellar structures appear to be maintained in the Y-form (compound **1** in the Y-form and an aqueous solution of **1** both show yellow photoluminescence). Though X-ray diffraction measurements were carried out for compound **1** in the Y-form to obtain further insight into the molecular assembled structures, no clear peaks were observed. This indicates that the micelles do not form sufficiently ordered structures to show clear X-ray diffraction after freeze-drying. Infrared spectral measurements provide information on the arrangement of the luminescent cores in micelles. In the Y-form, the amide groups of compound **1** are involved in hydrogen bond formation and no free amide C=O group is present (**Figure 8**, top), suggesting that the amide groups also play a role in hydrogen bonding in water. For a liquid-crystalline pyrene derivative having a similar molecular structure to **1**, a peak due to free amide C=O groups was observed at around 1680 cm^{-1}.[5c] It is noteworthy that hydrogen bonds were retained after grinding (Figure 8, bottom). Peaks corresponding to amide N-H stretching were not observed, because they were masked by the large and broad peaks ascribed to O-H stretching of compound **1**.

Based on the results described above, a schematic representation of the molecular assemblies of **1** in the micelles is shown in **Figure 9**. The pyrene moieties form segmented columnar

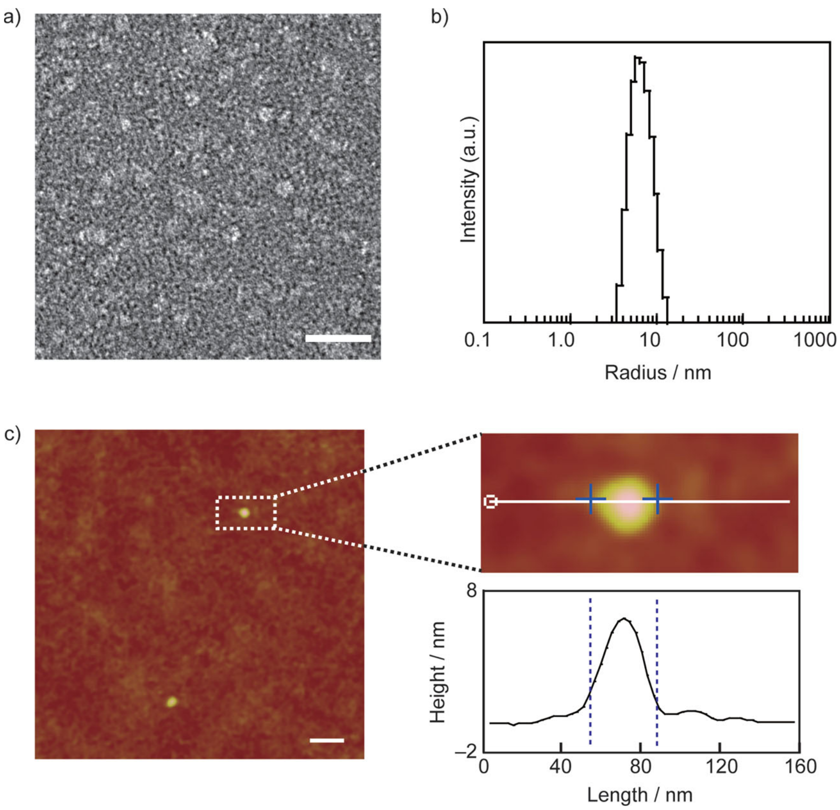

Figure 7. a) TEM image of the molecular assemblies of **1**. The sample was prepared by coating a dilute aqueous solution of **1** onto a copper grid and staining with uranyl acetate. Scale bar: 20 nm. b) Hydrodynamic radius distribution of the molecular assemblies of **1** in water at a concentration of 0.1 wt%, determined by dynamic light scattering measurement. c) AFM images of the molecular assemblies of **1**, together with the corresponding height profile. Samples were prepared by drop-casting a dilute aqueous solution of **1** onto a glass substrate. Scale bar: 100 nm.

structures surrounded by hydrophilic dendritic groups. All the hydroxyl groups of **1** are considered to be positioned at the surface of the micelles. In the segmented columnar structures, compound **1** should be present in disordered stacks, because the length between the H-bonded amide groups is generally longer than the distance between the adjacent luminescent cores that form π-stacked structures.[13] These molecular assemblies enable the micelles to dissolve in water and to exhibit yellow excimer emission. Micellar aggregates with anisotropy, like the micelles in this study, have been found for other amphiphilic molecules.[10] The formation of micelles in water in this study is consistent with the fact that some other dumbbell-shaped molecules have been reported to form micellar structures in the liquid-crystalline states.[5c,d,j] In the Y-form, compound **1** also forms the micellar structures.

2.4. Mechanism of the Photoluminescent Color Changes

Mechanical grinding induced changes in the arrangement of the luminescent cores, resulting in interference with normal excimer formation and leading to the appearance of green photoluminescence derived from partial-overlap excimers of the luminescent cores in the G-form. Because hydrogen bonds between the amide groups were retained after grinding (Figure 8, bottom), the luminescent cores are not separated sufficiently to show monomer emission. We speculate that exposure to RH = 100% may lead to an increase in the mobility of the peripheral hydrophilic moieties of the dendritic groups, allowing recovery of the initial micellar structures and yellow emission. This idea is supported by the fact that annealing of **1** in the G-form at 80 °C induced a red-shift of the emission spectrum (**Figure 10**). In other words, a thermally induced increase in the mobility of the dendritic moieties resulted in a structural change of the molecular assemblies, leading to a red shift of the emission band. For some mechanochromic luminescent

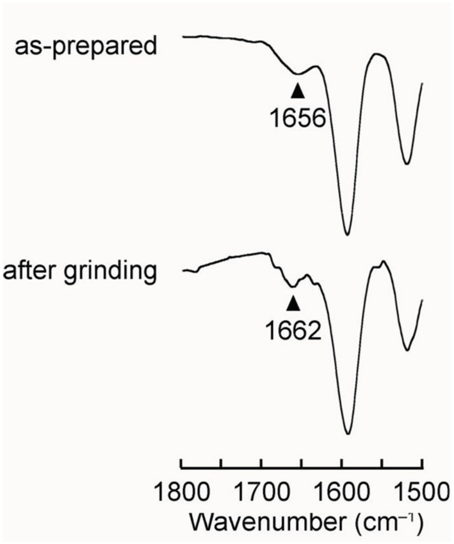

Figure 8. IR spectra of **1** as prepared (top) and **1** after grinding (bottom).

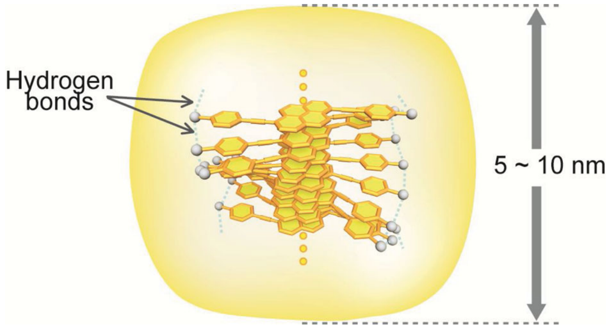

Figure 9. Schematic illustration of molecular assembly of pyrene derivative **1** into micelles. The dendritic groups of **1** are omitted in the illustration.

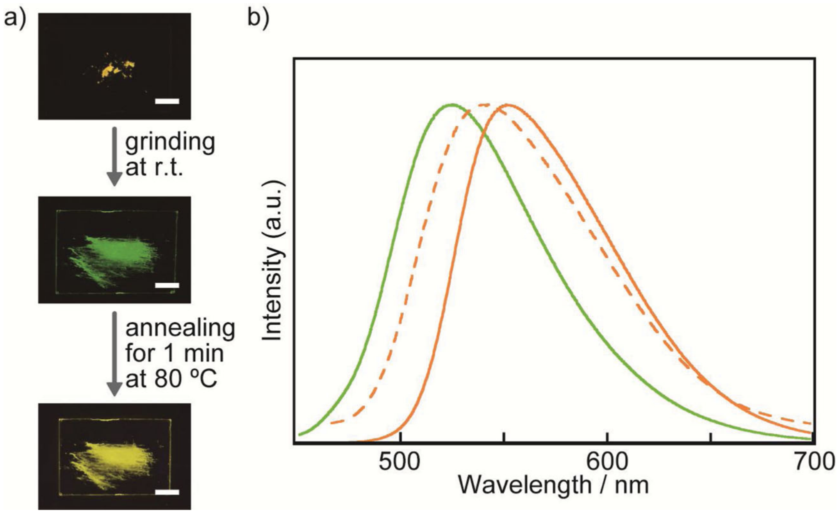

Figure 10. Recovery of the initial photoluminescence color through thermal treatment. a) Photoluminescence images of **1** on quartz substrates under UV irradiation at 365 nm. Scale bar: 5 mm. b) Photoluminescence spectra of compound **1** in the Y-form (RH < 5%, orange solid line), compound **1** after grinding (G-form) (RH < 5%, green solid line) and compound **1** after annealing of the G-form for 1 minute at 80 °C (RH < 5%, orange dotted line). λ_{ex} = 400 nm.

materials, the original photoluminescence properties are recovered upon exposure to vapors of organic solvents such as methylene chloride, chloroform, and tetrahydrofuran.[5e,g,i,o,p,q,6b,d] In such cases, the effective vapors are those of good solvents of the mechanochromically luminescent compounds. In the case of compound **1**, water is a good solvent, and thus the hydrophilic properties of the dendrons attached to the luminescent core may enable **1** to respond to high relative humidity.

2.5. Frictional Wear Testing for Grease

A typical application of water-soluble mechanochromic luminescent material is illustrated in **Figure 11** and Supporting Information Figure S5. Compound **1** is a suitable mechano-sensing material for application in frictional wear testing for grease, owing to its immiscibility in non-polar solvents and its non-crystalline behavior. A water solution of **1** was applied to a stainless steel plate, and the water was allowed to evaporate, leaving a thin film of compound **1** on the plate (Supporting Information Figure S5a). Subsequently, the surface was greased (Supporting Information Figure S5b), leaving the layer of compound **1** on the plate under a thin film of grease (Figure 11a). Most greases have no absorption in the visible region, so that the photoluminescence of compound **1** under the grease is easily detectable with the naked eye. Next, a stainless steel ball was placed in contact with the grease and rolled to-and-fro on the surface (Figure 11a, Supporting Information Figure S5c). Because compound **1** is immiscible with the grease, the thin film of compound **1** remained at the plate surface during this frictional wear test. As a result, the region where the thin film of grease was removed, i.e., the contact area between the plate and the ball, where the film of compound **1** was exposed to mechanical stimulation, was detected in terms of green photoluminescence of compound **1** (Figure 11b → 11c). In contrast, aliphatic compounds showing mechanochromic luminescence do not work in such frictional wear tests, as exemplified by pyrene-based liquid-crystalline compound **2**[5c] (**Figure 12**). As shown in Supporting Information Figure S6a, thin films of compound **2** were easily prepared on the stainless steel plate. But, when the surface was greased, the aliphatic pyrene derivative **2** was mixed with the grease (Supporting Information Figure S6b). Consequently, it was not possible to detect the region where mechanical stimulation was applied by using compound **2**.

3. Conclusion

In summary, we have found that the dumbbell-shaped pyrene derivative **1** exhibits mechanochromic luminescence; its photoluminescence color changes from yellow to green in response to mechanical grinding, and the initial yellow emission is recovered upon subsequent exposure to a high-humidity environment. Compound **1** is the first example of a mechanochromic luminescent organic compound that responds to relative humidity. This reversible switching of photoluminescence color is ascribed to the amphiphilic character of **1**, which forms micelles in water. Compound **1** was confirmed to be a suitable mechano-sensing material for application in frictional wear testing for grease, owing to its immiscibility in non-polar solvents and its non-crystalline

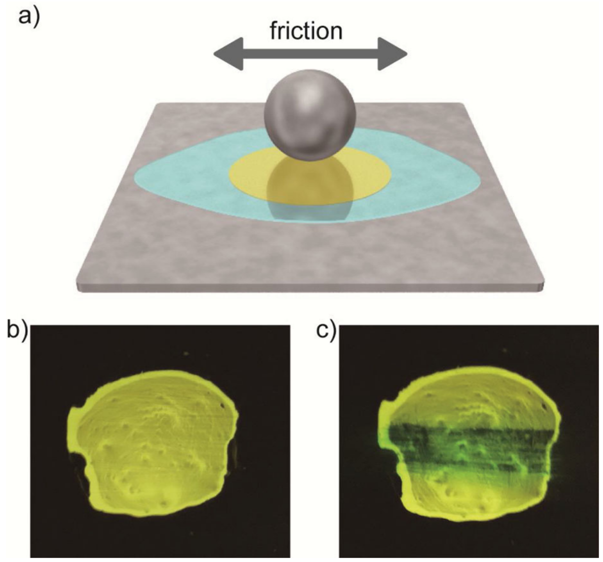

Figure 11. a) Schematic illustration of frictional wear test for grease. The yellow part represents the thin film of compound **1**. The blue part represents the thin film of grease. b) Photoluminescence image of compound **1** on the metallic plate under UV irradiation (365 nm). c) Photoluminescence image of compound **1** after the ball had been rolled to-and-fro.

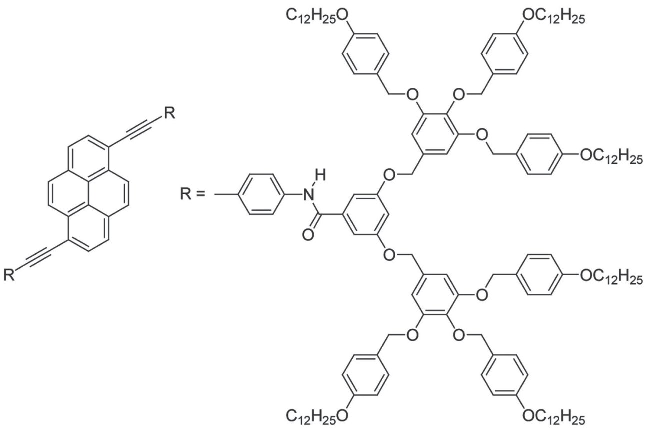

Figure 12. Molecular structure of an aliphatic pyrene derivative **2** exhibiting mechanochromic luminescence.

behavior. Water-soluble mechanochromic luminescent materials are also good candidates for molecular probes to detect various types of mechanical stimuli. Work to develop other types of water-soluble mechanochromic luminescent materials suitable for bioimaging is under way.

4. Experimental Section

Materials and Synthesis: All reagents and solvents were purchased from Aldrich, Tokyo Kasei, and Wako and appropriately purified, if necessary. Unless otherwise noted, all of the reactions were carried out under an argon atmosphere in dry solvents. Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical, 40–50 μm). Recycling preparative GPC was conducted with a Japan Analytical Industry LC-9210NEXT chromatograph.

General Procedures: ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-LA300 at 300 and 75 MHz, respectively. Chemical shifts of ^{1}H and ^{13}C NMR signals were referred to internal standard Me_4Si and expressed in ppm (δ), with multiplicity, coupling constant (Hz), and relative intensity. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu AXIMA-TOF^2 spectrometer. TEM images were obtained using a JEOL JEM-2100F. AFM images were recorded under ambient conditions using a Bruker BioScope Catalyst operating in the peak force tapping mode regime. Dynamic light scattering measurements were carried out using a HORIBA nano Partica SZ-100. IR measurements were conducted on a JASCO FT/IR-660 Plus with an ATR unit. UV-vis absorption spectra were measured with a Shimadzu UV-2550 spectrometer. Steady-state fluorescence spectra were recorded on a Hitachi F-7000 spectrofluorometer. Time-resolved fluorescence measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau. Quantum efficiencies were measured with a Hamamatsu Photonics Quantaurus-QY.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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