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Covalent Attachment of Mechanoresponsive Luminescent Micelles to Glasses and Polymers in Aqueous Conditions

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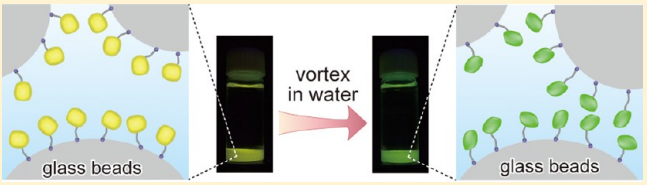
Supporting Information

ABSTRACT: Covalent attachment of mechanoresponsive luminescent organic or organometallic compounds to other materials is a promising approach to develop a wide variety of mechanoresponsive luminescent materials. Here, we report covalently linkable mechanoresponsive micelles that change their photoluminescence from yellow to green in response to mechanical stimulation under aqueous conditions. These micelles are composed of a dumbbell-shaped amphiphilic pyrene derivative having amine groups at the peripheral positions of its dendrons. Using a well-established cross-linker, the micelles were covalently linked via their peripheral amine groups to the surface of glass beads, polylactic acid (PLA) beads, and living cells under aqueous conditions. Vortexing of glass beads bearing the micelles in a glass vial filled with water caused a photoluminescence color change from yellow to green. PLA beads bearing the micelles showed no change in photoluminescence color under the same conditions. We ascribe this result to the lower density and stiffness of the PLA beads, because the color of the PLA beads changed on vortexing in the presence of bare glass beads. HeLa cells and HL-60 cells bearing the micelles showed no obvious photoluminescence color change under vortexing. The structure, photophysical properties, and mechanism of photoluminescence color change of the micellar assemblies were examined.



INTRODUCTION

Molecular materials that change their photophysical properties in response to mechanical stimulation are good candidates to visualize mechanical stresses that occur on or in many artificial materials, including industrially processed polymers, glasses, ceramics, and metals.[1] In the past decade, various compounds or polymers have been reported to exhibit mechanical stimulation-induced changes in photoluminescence color, and such materials have potential applications as sensors, memories, and information displays.[1,2] Various types of change in photoluminescence color have been observed for organic compounds,[3] metal complexes,[4] and polymers.[5] However, up to now, research has dealt primarily with the mechanoresponsive behavior of these materials, focusing on the relationship between photophysical properties and molecular structure. Moreover, mechano-responsive behavior has generally been observed in the ambient environment (in air) and on a relatively large scale (~mm). However, we are interested in finding ways to attach mechanoresponsive luminescent molecular assemblies to other materials of interest, such as glasses, polymers, and biomaterials, including living cells, sufficiently tightly to detect mechanical stress applied to these materials. Moreover, many potential applications would require a mechanoresponsive luminescent material that can function in aqueous conditions. So far, to our knowledge, there is no report of covalent bonding of mechanoresponsive luminescent molecular assemblies to other materials, or of such materials that function under aqueous conditions. It would also be desirable to develop materials that show distinct thresholds of mechanical power required to induce switching. This is difficult in the case of crystalline compounds, because the crystals are usually inhomogeneous in size. Though liquid crystals can form uniform thin films on the surfaces of other materials, strong mechanical shearing is likely to remove them, since they are not covalently bonded. Currently available mechanoresponsive polymeric materials are considered unsuitable for detecting low levels of mechanical stimulation, because rather high energy input is likely to be needed to extend or deform the polymeric materials sufficiently to achieve emission color changes.

Here, we show that mechanoresponsive luminescent micelles can overcome the difficulties facing practical application of previously reported mechanoresponsive luminescent materials. Our micelles have a uniform, small size (~6 nm) and appear to show a threshold of mechanical force for photoluminescence color change, although the threshold could not be quantitatively determined at present. Further, these micelles have peripheral amine groups that can be used to cross-link them covalently to various surfaces. Finally the photoluminescent color change occurs in an aqueous environment. We recently

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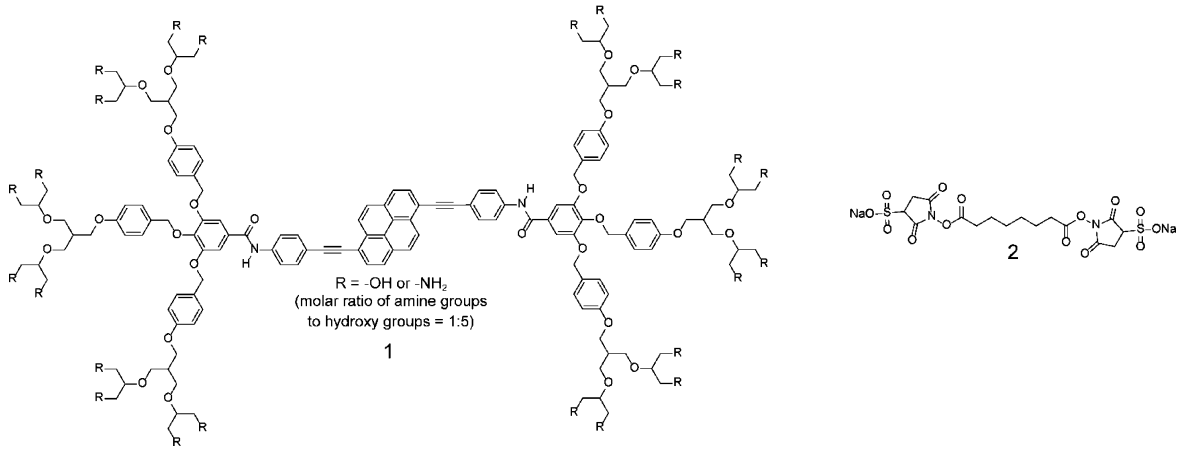
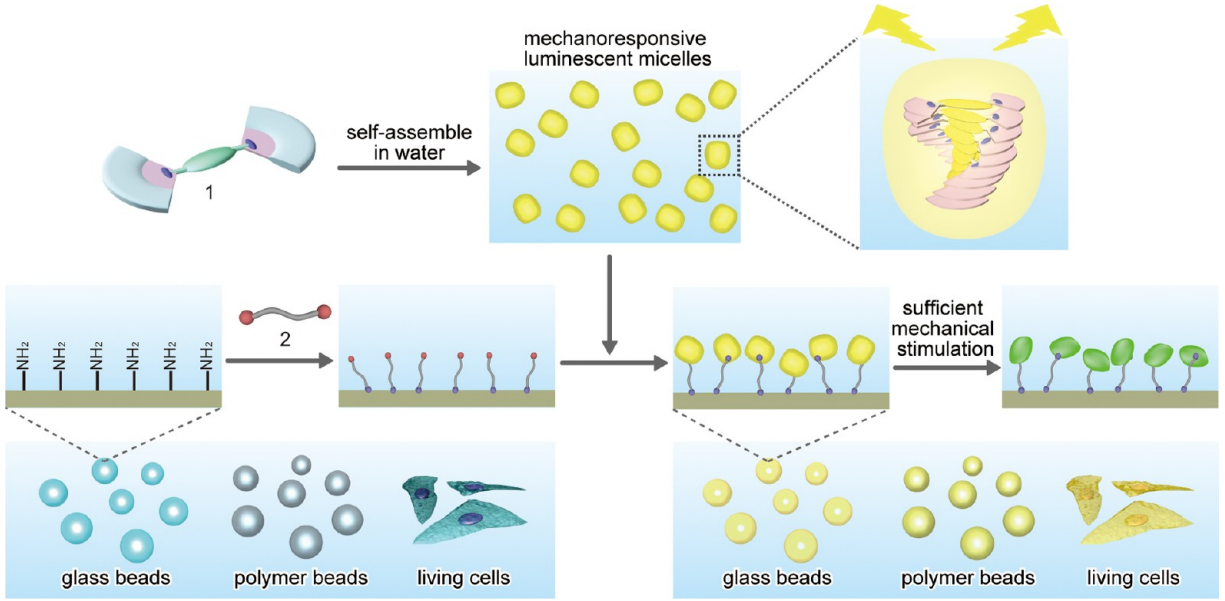
Scheme 1. Molecular Structures of Amphiphilic Pyrene Derivative 1 and Water-Soluble Cross-Linker 2



Scheme 2. Schematic Illustration of Covalent Attachment of Mechanoresponsive Micelles to Other Materials



reported an amphiphilic pyrene derivative with large dendritic structures that is water-soluble and switches its photoluminescent color in response to mechanical stimulation and change in relative humidity in the solid state.[6] However, that derivative does not show any photoluminescent color change under aqueous conditions, and was not covalently bonded to other materials.

RESULTS AND DISCUSSION

Molecular Designs and Synthesis. A dumbbell-shaped, amphiphilic pyrene derivative **1** (Scheme 1) was designed and synthesized by tosylation, azidation, and subsequent Staudinger reaction of hydroxy groups at peripheral positions of compound **12** (see Supporting Information [SI]). Conversion from hydroxyl groups to amine groups was confirmed by the MALDI-TOF-MS spectra (Figure S1 in SI), as well as ^{1}H NMR and ^{13}C NMR spectra. The molar ratio of amine groups to hydroxy groups is approximately 0.2 for compound **1**, as determined by ^{1}H NMR.

It is well-known that amphiphilic molecules having rigid aromatic moieties and flexible hydrophilic groups can self-assemble into a wide variety of structures, including spherical micelles, cylindrical micelles, hollow vesicles, and planar membranes, in aqueous solvents.[7] In addition, some dumbbell-shaped compounds have been found to exhibit mechanochromic luminescence.[1b,3c,d,g,h,6] Therefore, dumbbell-shaped amphiphile **1** was expected to form aggregates under aqueous conditions and to exhibit mechanoresponsive behavior. Building on our previous pyrene derivative (see Figure S2 in SI), which carries large hydrophilic dendritic structures[8] and shows no photoluminescent color change in aqueous conditions,[6] we designed compound **1** with smaller hydrophilic dendrons, which we hoped would readily adopt bistable states that could be switched by mechanical stimulation in aqueous conditions. We also introduced two amide groups between the luminescent core and the dendrons. The use of noncovalent intermolecular interactions such as hydrogen bonds is known to be a promising way to align luminophores for building sophisticated photofunctional materials.[1b,3a,c,d,g,h,6,9] Moreover, we adopted the water-soluble cross-linker **2** (Scheme 1), which has amine-reactive *N*-hydroxysulfosuccinimide ester groups at both ends.

Design Concept. Scheme 2 is a schematic illustration showing covalent attachment of mechanoresponsive micelles to

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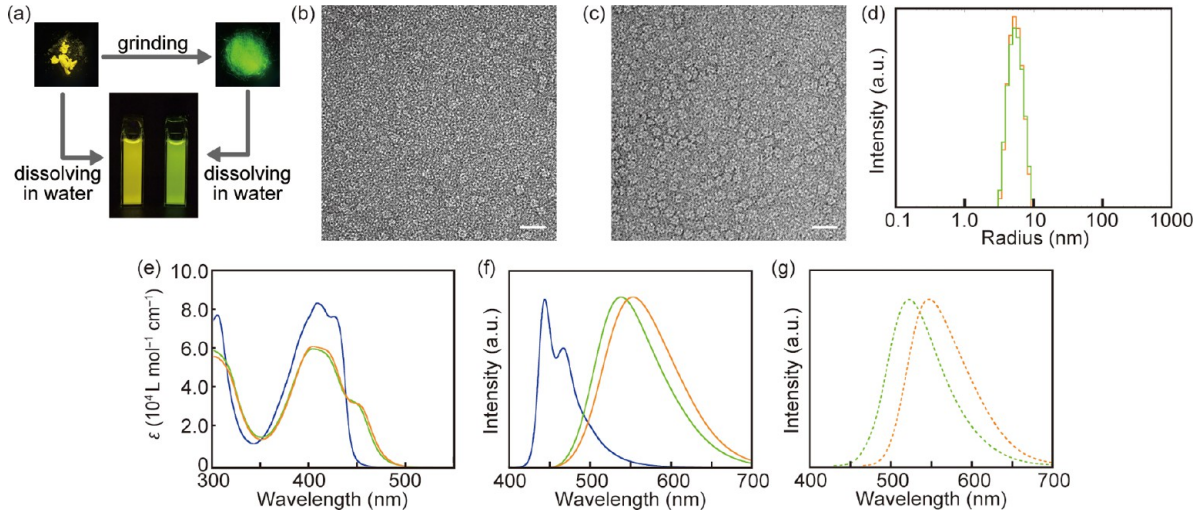

Figure 1. (a) The top two images are photoluminescence images of compound **1** before and after grinding in the solid state. The images were taken on quartz substrates. The bottom image shows the photoluminescence of water solutions of Y-micelles (left) and G-micelles (right) in the optical quartz cells. λ_{ex} = 365 nm. (b, c) Transmission electron microscope images of Y-micelles and G-micelles. Scale bar: 20 nm. (d) Hydrodynamic radius distributions of Y-micelles (orange line) and G-micelles (green line) in water determined by dynamic light-scattering measurements. (e, f) Absorption and photoluminescence spectra of **1** in methanol (blue line), water solution of Y-micelles (orange line) and water solution of G-micelles (green line). Concentrations of compound **1** were 1.0×10^{-5} M. λ_{ex} = 400 nm. (g) Photoluminescence spectra of compound **1** in the solid state before (orange dotted line) and after (green dotted line) grinding. λ_{ex} = 400 nm.

other materials. Compound **1** was expected to form micelles under aqueous conditions because of its amphiphilic properties, as was the case with the pyrene derivative in our previous study.[6] The resultant micelles were also expected to exhibit yellow emission due to excimer[10] emission of the 1,6-diethynylpyrene[11] moiety. Many amine and hydroxy groups were expected to be located at the exterior of the micelles under aqueous conditions. By using a water-soluble cross-linker **2**, the micelles can be covalently bonded to glass, polymers or other materials with amine groups on their surfaces. Because living cells have many amine groups in membrane proteins, they should also be available as targets of these micelles. We anticipated that mechanical stimulation applied to the covalently bound mechanoresponsive micelles would cause a change of photoluminescence color. Further, because the micelles are highly uniform in size, there might be a threshold of stimulation for color change, potentially enabling us to evaluate the magnitude of the applied mechanical force.

Bistable Molecular Assembled States under Aqueous Conditions. Compound **1** was obtained as yellow cottony solid that exhibits yellow photoluminescence under excitation light (Figure 1a, top left). In the solid state, the photoluminescence color changed from yellow to green in response to mechanical grinding (Figure 1a, top left → top right). Compound **1** in the initial yellow state dissolves in water, and the resultant solution also shows yellow photoluminescence (Figure 1a, bottom left). On the other hand, when green photoluminescence-emitting ground **1** was dissolved in water, green photoluminescence was observed under excitation (Figure 1a, bottom right). These observations indicate that compound **1** forms two different molecular assembled states in aqueous conditions and imply that mechanical stimulation induces a change in the assembled state under aqueous conditions. In contrast, it is noteworthy that the pyrene derivative in our previous study exhibited complete recovery of the initial photoluminescence color when it was dissolved in water after mechanical grinding in the solid state.[6] We consider that a decrease in the volume of the hydrophilic dendritic structures attached to the luminescent cores enables compound **1** to form two different assembled states in aqueous conditions. Slight changes in molecular structure are often sufficient to cause significant changes of external stimulus-responsive behavior of molecular assembled materials.

To examine the two forms of molecular assemblies of **1**, transmission electron microscopy was carried out. As shown in b and c of Figure1 and Figures S3 and S4 in SI, many spherical structures with uniform diameter (∼ 6 nm) can be seen, suggesting that compound **1** forms micelles in water in both forms. The diameters of the yellow-emitting micelles (Y-micelles) and the green-emitting micelles (G-micelles) were consistent with the molecular length of **1** (∼6 nm). Dynamic light scattering (DLS) measurements (Figure 1d) supported the existence of micellar aggregates of compound **1** in both cases. The average hydrodynamic radius was approximately 5 nm in both cases (Figure 1d), which is roughly consistent with the observed diameter of micelles in the TEM images. The results obtained from infrared spectral measurements indicate that the amide groups of compound **1** are involved in hydrogen bonding in Y- and G-micelles (Figure S5 in SI).

The photophysical properties of **1** were examined to clarify the mechanism of the photoluminescence color change. The absorption and photoluminescence spectra of compound **1** in methanol (1.0×10^{-5} M) showed vibronic structures (e and f of Figure 1, blue lines) and only one emission species (1.0 ns) was observed in emission lifetime measurements (Table 1), indicating that compound **1** is in the monomeric state in methanol. The absorptions of the yellow- and green-emitting water solutions (Figure 1e, orange and green lines) are broadened and red-shifted compared to that of the methanol solution of **1**. These spectral data suggest that ground-state electronic interactions between the luminescent groups occur in Y- and G-micelles. As the absorption spectrum of Y-micelles in water does not completely coincide with that of G-micelles in water, the arrangement of the luminescent cores should be

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Table 1. Emission Lifetimes and Quantum Yields[a,b]

	τ_i (amplitude a_i) (ns)	τ_{av}[c] (ns)	X^2	Φ_{PL}
1 in methanol (λ_{em} = 445 nm)	1.0 (100%)	1.0	1.08	0.64
Y-micelles in water (λ_{em} = 540 nm)	5.4 (35%), 39 (45%), 90 (20%)	61	1.10	0.42
Y-micelles in water (λ_{em} = 600 nm)	6.5 (20%), 44 (50%), 90 (30%)	69	1.08	
G-micelles in water (λ_{em} = 540 nm)	6.2 (52%), 26 (39%), 85 (9%)	44	1.18	0.47
G-micelles in water (λ_{em} = 600 nm)	7.8 (43%), 31 (41%), 85(16%)	53	1.04	

[a]All measurements were carried out under ambient conditions. [b]Emission decay profiles are shown in Figures S6 and S7. [c]Average lifetimes were calculated using the following formula: $\tau_{av}=(\sum a_i\tau_i^2)/(\sum a_i\tau_i)$

slightly different in the two forms. As shown in Figure 1f, the emission spectra of Y- and G-micelles in water are very broad and structureless. The emission bands are significantly red-shifted compared to that of the methanol solution of **1**, indicating that the emissions result from molecular assemblies. The emission spectrum of Y-micelles in water displays a peak at 554 nm, while the emission spectrum of G-micelles in water displays a peak at 542 nm. It is noteworthy that the emission peak for ground **1** in the solid state appears at 524 nm (Figure 1g, green dotted line). Thus, dissolution in water results in a change in the arrangements of the luminophores, though the precise nature of the molecular assembled structures was not clarified for ground **1**.

To obtain more insight into the difference in photoluminescence color between Y- and G-micelles in water, emission lifetime measurements were carried out for water solutions of Y-micelles and G-micelles, as well as a methanol solution of compound **1** (Table 1). Emission decay profiles of water solutions of Y- and G-micelles were obtained at 540 and 600 nm (Figures S6 and S7 in SI). The complex fluorescence decay profiles were fitted to triple exponential decay curves, though more emission species seemed to exist in both cases. Different from those of crystalline compounds, the emission cores are fixed in several arrangements that are different from each other in soft materials like the micelles in this study. For both water solutions, the proportions of emission species with long lifetimes at 600 nm are larger than those observed at 540 nm. These results indicate that, as the emission wavelength gets longer, the emission lifetime increases. Comparison of the results obtained for Y-micelles in water with those for G-micelles in water indicates that the change in the proportion of emission species results in the difference in photoluminescence spectra between water solutions of Y- and G-micelles. The emission species with long emission lifetimes can be assigned as excimers[10] of the luminescent cores. Excimers with long lifetimes have been observed in our previous studies.[3c,d,g,h,6] The quantum efficiencies of water solutions of Y-micelles and G-micelles were 0.42 and 0.47, respectively (Table 1). These values are sufficient for practical applications.

Taking all of the above experimental data into account, we propose that the molecular assemblies in the Y-micelles are as shown in Scheme 2 (top right), with the hydrophobic parts of compound **1** stacked to form disordered segmented columns and the amide groups forming hydrogen bonds between adjacent molecules. Because of the bulkiness of the hydrophilic dendritic structures of **1**, the hydrophobic parts of **1** do not form nonsegmented columnar structures. Therefore, compound **1** forms anisotropic micellar aggregates. Similar anisotropic micelles have been reported for other amphiphilic molecules.[12] We have also shown that some dumbbell-shaped molecules form such molecular assemblies.[3c,d,g,h,6] The molecular assemblies of Y-micelles enable the luminescent cores to form excimers, resulting in yellow photoluminescence.

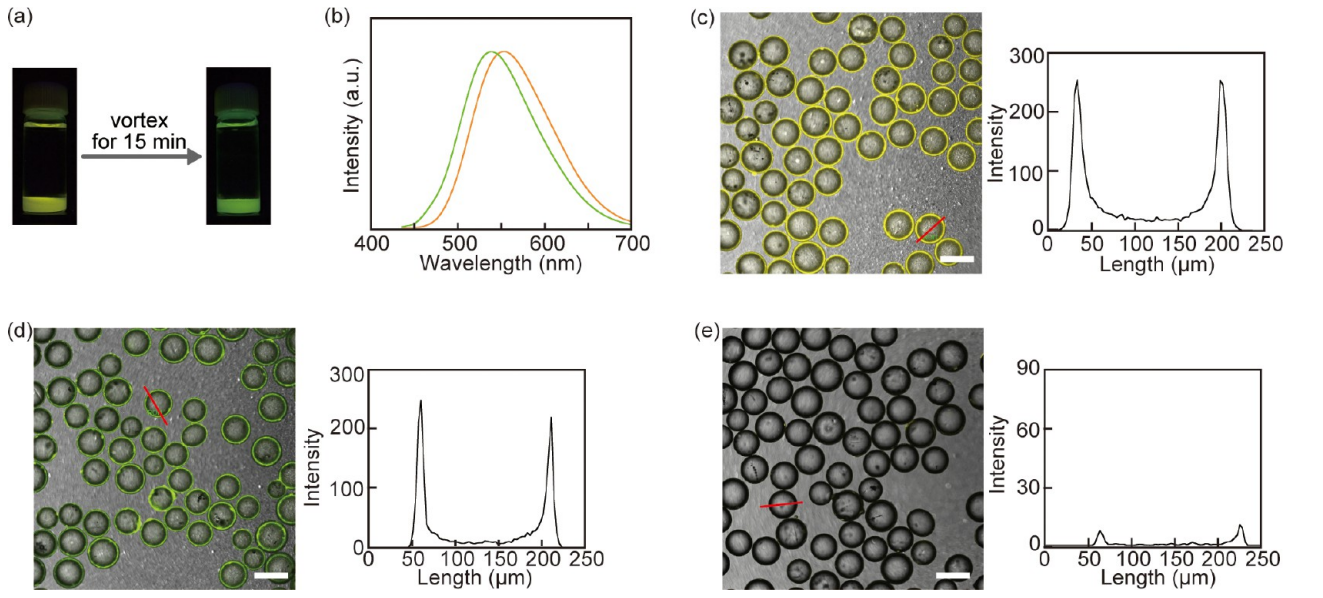

Figure 2. (a) Change in the photoluminescence color of glass beads (Φ = 150−212 μm) covered with covalently bonded micelles in response to mechanical stimulation (vortexing at 2000 rpm). Glass beads are in glass vials filled with water. λ_{ex} = 365 nm. (b) Photoluminescence spectra of glass beads with micelles before (orange line) and after (green line) vortexing in water. (c, d) Confocal fluorescence microscopic images of glass beads bearing micelles before and after vortexing, together with the emission intensity profile along the red line in the image. (e) Confocal fluorescent microscopic image of glass beads subjected to the attachment procedure but without cross-linker **2**. Scale bar: 200 μm. The images were taken under the same conditions.

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In G-micelles, the arrangements of the luminescent cores are slightly different, resulting in a decrease in the proportion of emission species with longer emission lifetimes, thereby leading to the change in photoluminescence color.

Attachment of Micelles to Glass Beads. As compound **1** was found to form bistable molecular assembled states in water, we attached Y-micelles to glass beads (Φ = 150−212 μm) using cross-linker **2**. Phosphate-buffered saline (PBS, pH = 7.4) was used to maintain the pH at the desired value for reaction between amine groups and *N*-hydroxysulfosuccinimide ester groups of compound **2** under aqueous conditions. Y- and G-micelles show the same photoluminescence colors in water and in PBS. Before attachment of Y-micelles to glass beads, amine groups were introduced onto the glass beads via silane coupling reaction.[13] After binding of Y-micelles, glass beads exhibited yellow photoluminescence in water under excitation light (λ_{ex} = 365 nm) (Figure 2a, left). The emission spectrum of Y-micelles attached to glass beads in water (Figure 2b, orange line) coincides almost exactly with that of a water solution of Y-micelles, indicating that the molecular assemblies were unaffected by the attachment procedures. Figure 2c shows a confocal fluorescence microscopic image of glass beads bearing Y-micelles, which confirms that the micelles are located at the surface of the glass beads. Such covalent bonding is difficult to achieve with mechanoresponsive organic or organometallic crystals.

When the glass vial containing glass beads bearing Y-micelles in water was vortexed at 2000 rpm at room temperature for 15 min, the photoluminescence color changed from yellow to green (Figure 2a). The emission spectrum of the glass beads after vortexing (Figure 2b, green line) is very similar to that of G-micelles in water (Figure 1f, green line). The confocal fluorescence microscopic image (Figure 2d) confirms that covalently bonded micelles were not removed from the surface of the glass beads during the vortexing procedure. These results mean that mechanical stress during vortexing induced transformation of Y-micelles to G-micelles on the surface of the glass beads. It should be noted that few micelles were adsorbed on the surfaces of glass beads in the absence of covalent linking via cross-linker **2** (Figure 2e).

As shown in Figure 3, we conducted the same experiments using smaller glass beads (Φ < 106 μm) than those used in Figure 2. Y-micelles were again covalently attached to the surface of the glass beads using cross-linker **2**, as confirmed by the photoluminescence spectrum (Figure 3b, orange line) and by confocal fluorescence microscopic imaging (Figure 3c). However, different from the former glass beads (Φ = 150−212 μm), it took one hour to achieve complete transition of the photoluminescence color, even though the glass beads were vortexed under the same conditions as in Figure 2. The emission band shows a gradual blue-shift over time (Figure 3b). As the diameters of the glass beads (Φ < 106 μm) are smaller than those of the glass beads used in Figure 2, the mechanical forces involved in interbead collisions during vortexing would be smaller than in the case of Figure 2. Again, the confocal fluorescence microscopic image confirmed that the micelles were not lost during vortexing (Figure 3d).

Attachment of Micelles to Polymer Beads. To confirm that the Y-micelles can also be attached to other materials with retention of mechanoresponsive luminescence properties, we attached Y-micelles to polylactic acid (PLA) beads (Φ = 70−150 μm) with amino groups on their surfaces. After introduction of Y-micelles onto the PLA beads, yellow photoluminescence was seen in water (Figure 4a, left). The emission spectrum (Figure 4b, orange solid line) and confocal

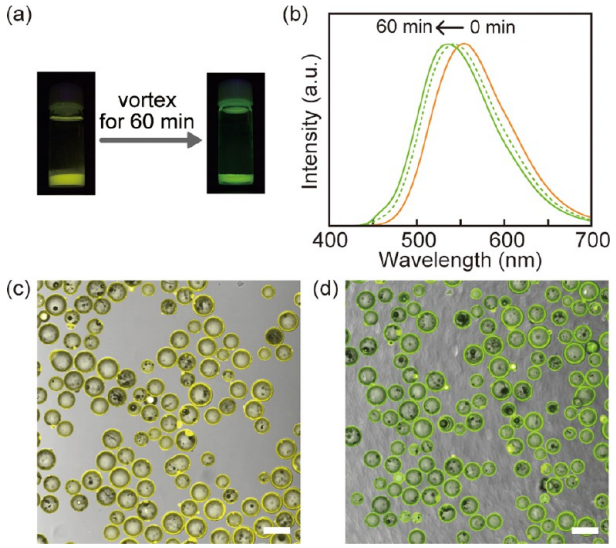

Figure 3. (a) Change in the photoluminescence color of glass beads (Φ < 106 μm) bearing covalently bonded micelles in response to mechanical stimulation in water. The beads are in glass vials filled with water. λ_{ex} = 365 nm. Rotational frequency: 2000 rpm. (b) Photoluminescence spectra of glass beads bearing micelles in water before vortexing (orange line), after vortexing for 30 min (green dotted line) and after vortexing for 60 min (green solid line). (c, d) Confocal fluorescence microscopic images of glass beads bearing micelles before and after vortexing. Scale bar: 100 μm. The images were taken under the same conditions.

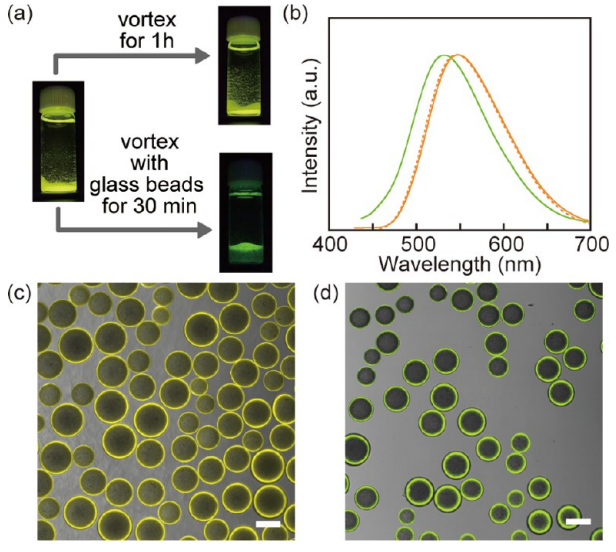

Figure 4. (a) Change in the photoluminescence color of PLA beads bearing covalently bonded micelles in response to mechanical stimulations in water. The glass vial in the bottom right image contains bare glass beads as well as micelle-bonded PLA beads. λ_{ex} = 365 nm. Rotational frequency: 2000 rpm. (b) Photoluminescence spectra of PLA beads bearing covalently linked micelles in water before vortexing (orange solid line), after vortexing for 1 h without glass beads (orange dotted line) and after vortexing for 30 min in the presence of bare glass beads (green solid line). (c, d) Confocal fluorescence microscopic images of PLA beads with micelles before and after vortexing with glass beads. Scale bar: 100 μm. The images were taken under the same conditions.

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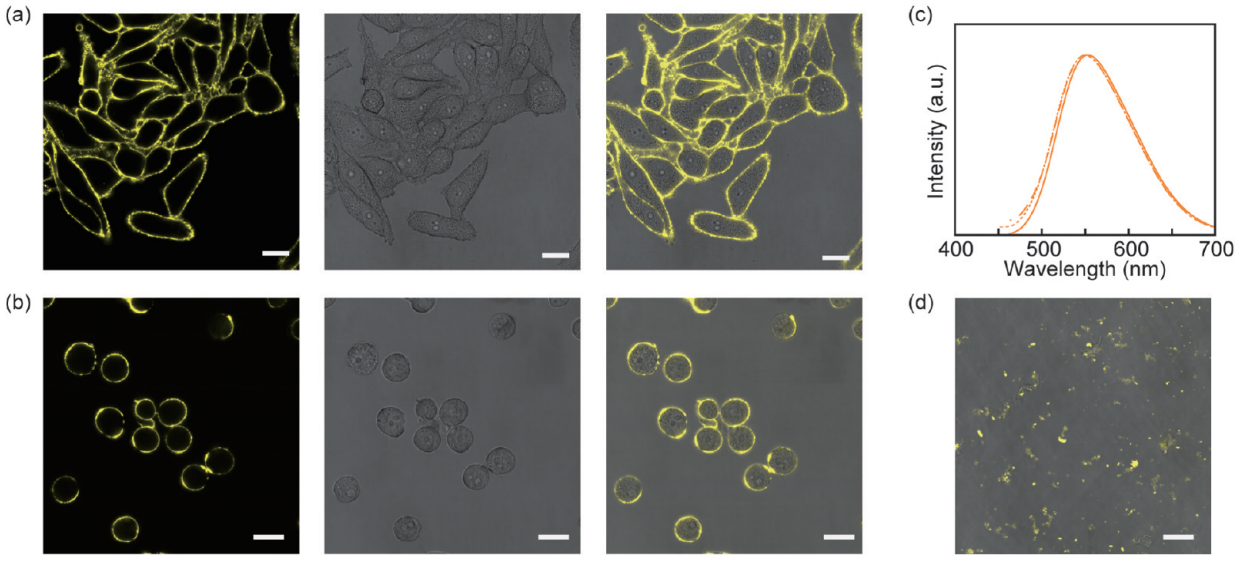

Figure 5. Confocal fluorescence microscopic images of (a) HeLa cells and (b) HL-60 cells loaded with Y-micelles, showing fluorescence image (left), bright-field image (center) and merged image (right). (c) Photoluminescence spectra of HL-60 cells with micelles in Hank's balanced salt solution (HBSS) before vortexing (orange solid line), after vortexing for 1 h without glass beads (orange dotted line) and after vortexing for 1 h with bare glass beads (orange broken line). (d) Confocal microscopic merged image of broken HL-60 cells bearing micelles after vortexing with glass beads. Scale bar: 20 μm.

fluorescence microscopic image (Figure 4c) indicate that Y-micelles had been introduced at the surface of PLA beads without change of the photoluminescence properties in water. Different from the case of the glass beads, vortexing for 1 h in water (2000 rpm) induced no change in the photoluminescence color of the PLA beads (Figure 4a, left → top right). The emission spectrum also showed no obvious change (Figure 4b, orange solid line → orange dotted line). However, luminescence color change of the PLA beads occurred during vortexing with large glass beads (Φ = 425−600 μm) in water for 30 min (Figure 4a, left→ bottom right), as confirmed by emission spectral measurements (Figure 4b, orange solid line → green solid line). As shown in Figure 4d, the micelles were not detached from the glass beads during vortexing.

The difference in sensitivity to mechanical stimulation between glass and PLA beads is considered to result from the differences in density and stiffness between the two types of beads. The densities of the glass and PLA beads were 2.5 g cm^{-3} and 1.0 g cm^{-3}, respectively. Since glass beads are heavier than PLA beads of the same size, the mechanical force applied to Y-micelles on the surfaces of colliding glass beads would be greater than that in the case of PLA beads. Moreover, the stiffness of glass beads is much larger than that of PLA beads. It is noteworthy that green photoluminescence was not detected from PLA beads after vortexing with small glass beads (Φ < 106 μm) for 1 h. These results indicate that there is a threshold level of mechanical stimulation to induce transformation from Y-micelles to G-micelles. The existence of a threshold is considered to reflect the fact that Y-micelles have uniform size (b and d of Figure 1).

Among polymeric materials that have been reported to show mechanoresponsive luminescent behavior, the extension of polymer molecules is required to change the photoluminescence color.[1a,e,f,5] In such polymer-based materials, the extension results in molecular structural change of mechanophores or dissociation of aggregated luminophores, leading to the photoluminescence color changes. In contrast to such conventional polymer-based materials, our PLA beads bearing Y-micelles in this study showed a photoluminescence color change that did not rely on deformation of the PLA beads. The micelle-bearing PLA beads therefore represent a new type of polymer-based mechanoresponsive luminescent material.

Attachment of Micelles to Living Cells. To confirm that the Y-micelles can also be attached to biomaterials as well as glass and polymer beads, Y-micelles were covalently bonded to amine groups on plasma membranes of living cells in Hank's balanced salt solution (HBSS) with retention of the molecular assembly structures and the yellow photoluminescence color. Figure 5a shows confocal fluorescence microscopic images of HeLa cells bearing Y-micelles, indicating that Y-micelles are good candidates for molecular probes to image the plasma membrane. Y-Micelles are quite large (6 nm) compared to widely used membrane-permeable fluorescence probes,[14] and are not membrane permeable, so high-contrast images of the plasma membrane can be obtained, provided that cellular uptake through endocytosis is suppressed. As shown in Figure 5b, Y-micelles were also attached to plasma membranes of floating HL-60 cells, as well as adherent HeLa cells. The emission spectrum of HL-60 cells bearing Y-micelles (Figure 5c, orange line) coincides with those of the Y-micelle-bearing glass and PLA beads before vortexing. Finally, HL-60 cells were subjected to vortexing (2000 rpm, in HBSS). As might have been expected, transition from Y-micelles to G-micelles was not detected after vortexing for 1 h (Figure 5c, orange dotted line). Because our micelles have a threshold of mechanical force for induction of photoluminescence color changes, tiny mechanical powers between cells during vortexing result in no obvious photoluminescence color changes. HL-60 cells bearing Y-micelles were also subjected to vortexing (2000 rpm, in HBSS) in the presence of large glass beads. However, any photoluminescence changes were not observed again (Figure 5c, orange broken line). Confocal fluorescence microscopic observation revealed that HL-60 cells were disrupted by vortexing with glass beads (Figure 5d). Our hypothesis is that Y-micelles were buried in the large and small pieces of shattered

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cells, which prevents Y-micelles exhibiting transition to G-micelles during vortexing with large glass beads.

CONCLUSION

We have prepared mechanoresponsive luminescent micelles, composed of dumbbell-shaped amphiphile **1**, that exhibit transformation from Y-micelles to G-micelles in response to mechanical stimulation in aqueous conditions concomitantly with a photoluminescence color change from yellow to green. By using our micelles, many kinds of materials can be given mechano-sensing capability. The micelles were covalently linked to glass beads, PLA beads, and living cells via their amine groups by using cross-linker **2**. On both glass and PLA beads, Y-micelles covalently attached to the surface of beads were transformed to G-micelles when sufficient mechanical stimulation was applied. In contrast, Y-micelles covalently attached to plasma membranes of HL-60 cells never showed transition to G-micelles. The micelles appear to have a threshold of mechanical power for induction of photoluminescence color change, probably because of their uniform size, though the threshold remains to be quantitatively evaluated.

Compound **1** is the first example of mechanoresponsive luminescent micelles that work in water and the first example of a mechanoresponsive luminescent molecular assembly that works when covalently bonded to a substrate. The threshold of mechanical power for induction of photoluminescence color change depends on the molecular structure itself and the molecular assembled structures. Further work is under way in our laboratory to develop several types of mechano-sensitive micelles with sensitivities different from that of Y-micelles.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization data of compound **1**, additional TEM images, IR spectra, emission decay profiles, and confocal fluorescent microscopic images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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