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Mechanochromic luminescence of phase-separated hydrogels that contain cyclophane mechanophores

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Mechanochromic mechanophores which are covalently introduced into polymer materials can visualize the mechanical force applied to the polymer chains. Mechanochromic hydrogels using mechanophores such as 1,2-dioxetane derivative, spiropyran, and rhodamine have been developed so far. However, these hydrogels do not show instant reversibility in response to force because scission of covalent bonds is needed for the mechanophores for activation. Here, mechanochromic luminescent hydrogels that show reversible changes of emission properties are demonstrated utilizing a cyclophane-based supramolecular mechanophore whose working mechanism does not rely on breakage of covalent bonds. The cyclophane mechanophore is introduced into phase-separated hydrogels as a crosslinker. The decrease in intramolecular excimers upon deformation results in the mechanochromic luminescence and the emission change was achieved reversibly and instantly. It was also found that most of the mechanophores are incorporated in the hydrophobic part of the hydrogels, when replacing dimethylsulfoxide with water in gels.

Introduction

Hydrogels have several potential applications, including in soft electronic devices, soft robots, and tissue engineering.[1–3] The incorporation of a mechanism that enables the evaluation and visualisation of mechanical stimuli applied to hydrogels would be useful for understanding the nanomechanics in hydrogels, leading to longer lifetimes. Over the years, several mechanochromic hydrogels have been developed using fluorescence resonance energy transfer (FRET) pairs,[4] polarity-sensing dyes such as 8-anilino-1-naphthalenesulfonic acid (ANS),[5] dye grafted prepolymer,[6] aggregation of fluorophores,[7] or structural colour change.[8] The introduction of mechanochromic mechanophores is another promising method for studying the force applied to polymer chains in hydrogels.[9–16] For instance, Zheng et al. introduced spiropyran (SP) groups into hydrogels by utilizing surfactants.[9] The SP moieties in hydrogels were converted to merocyanine (MC) by stretching to 300% strain, heating, or irradiating the hydrogels with ultraviolet (UV) light. After the conversion to MC, recovery of

the SP groups requires white-light irradiation. Yang et al. incorporated rhodamine mechanophores into a rigid and brittle network in double-network hydrogels to achieve autonomous reversibility.[15] The hydrogel changed its emission colour from blue to orange upon deformation to 100% strain and slowly recovered its initial state without any external stimuli after relaxing. However, the irreversible or slowly reversible change in the photophysical properties, which inherently results from the scission of covalent bonds in the mechanophores, makes them unsuitable for *in situ* visualisation of the applied force. Therefore, mechanophores which are activated without any cleavage of covalent bonds and exhibit instantly reversible changes in photophysical properties are preferable.[16–28] For instance, a flapping molecule with a cyclooctatetraene moiety and two pyreneimide wings functions as a force probe in the polyurethane organogel and visualises the force distribution using a hyperspectral camera.[24]

Supramolecular mechanophores,[16–22] which change their photophysical properties based on the alteration of the assembly states of luminophores and/or quenchers, are also promising candidates for *in situ* investigations because of their instantly reversible nature. Supramolecular mechanophores with rotaxane,[16–18] cyclophane,[19,20] or loop[21,22] motifs have been developed to show significant enhancement of the fluorescence intensity or ratiometric fluorescence colour changes in polymer films. Such supramolecular mechanophores are useful for detecting small forces arising in hydrogels. Indeed, a rotaxane-based supramolecular mechanophore involving the FRET mechanism exhibits reversible changes in the red emission intensity upon stretching and relaxation of the poly(urethane-urea) hydrogel in which the mechanophore is covalently embedded.[16] However, simply changing the emission intensity

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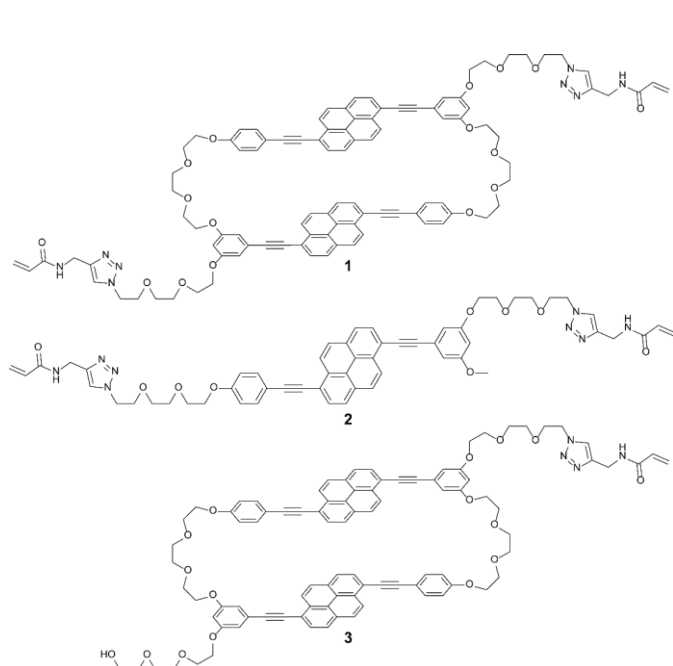
Fig.1 Molecular structures of cyclophane mechanophore **1**, monomer analogue **2**, and mono-functionalized cyclophane **3**.

Scheme 1 Synthesis of cyclophane mechanophore **1**.

makes it difficult to quantitatively evaluate the force applied to hydrogels because emission intensities are affected by differences in the local mechanophore concentrations. Therefore, mechanophores that exhibit ratiometric changes in emission are preferred for examining the detailed distribution of forces in hydrogels.

In this study, we demonstrate that hydrogels exhibiting ratiometric changes in fluorescence upon stretching can be developed by covalently embedding cyclophane-based supramolecular mechanophores at cross-linking points of phase-separated hydrogels.

Results and discussion

Cyclophane mechanophore **1** and monomer analogue **2** were designed to have two acrylamide groups at the ends so that the compounds are covalently introduced into hydrogels as

crosslinkers (Fig. 1). The molecular structure of compound **1** is based on our previous cyclophane mechanophore **4** that exhibits instantly reversible, ratiometric fluorescence colour changes when embedded in a linear segmented polyurethane elastomer.[19] Cyclophane **1** was expected to form an intramolecular excimer in the force-free state. Because reference compound **2** has one fluorophore, it exhibits only monomer emissions when used at low concentrations. Compound **3** is a reference cyclophane with only one acrylamide group.

A reported cyclophane mechanophore, compound **4**,[19] was used to synthesize **1**. Two hydroxyl groups at the ends of compound **4** were converted (Scheme 1) to tosyl groups through a reaction with *p*-toluenesulfonyl chloride to afford compound **5**, which was subsequently reacted with sodium azide to form compound **6**. Then, a CuAAC click reaction was performed between compound **6** and *N*-propargylacrylamide,
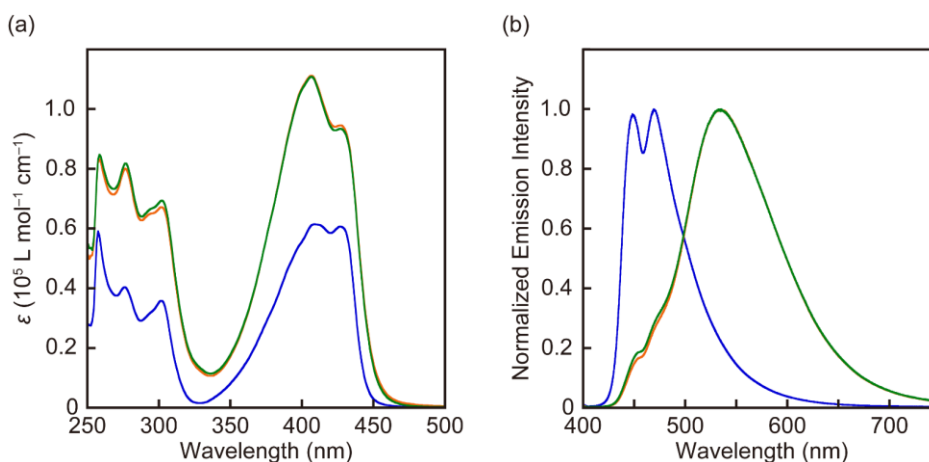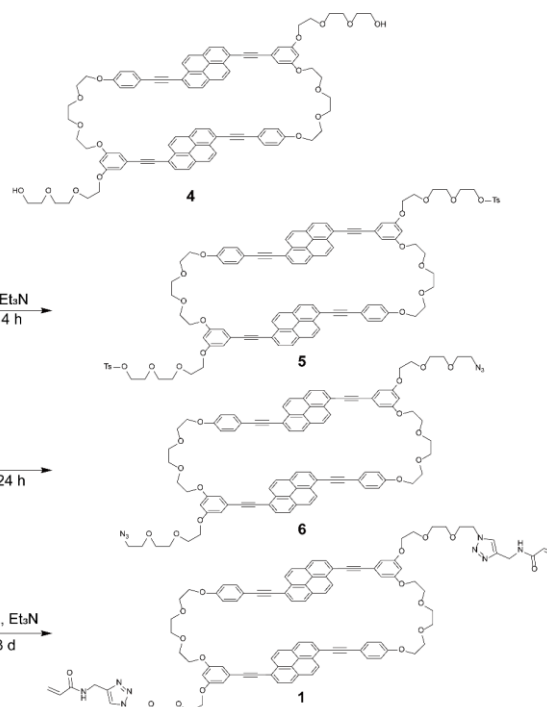

Fig. 2 (a) UV-vis absorption and (b) photoluminescence spectra of mechanophore **1** (green line), compound **2** (blue line), and compound **3** (orange line) in DMSO (*c* = 1.0 × 10^{-5} M). The excitation wavelength was 400 nm.

to obtain cyclophane mechanophore **1** (see the ESI† for details). Compounds **2** and **3** were also synthesised as shown in Schemes S1 and S2 and characterised through ^{1}H and ^{13}C NMR spectroscopy and high-resolution electrospray ionisation mass spectrometry (see the ESI† for details).

The photophysical properties of **1**–**3** were investigated in dimethylsulfoxide (DMSO) ($c = 1.0 \times 10^{-5}$ M) (Fig. 2). The DMSO solution of **2** shows an absorption spectrum with maxima at 409 nm ($\varepsilon = 6.1 \times 10^4$ L mol^{-1} cm^{-1}) and 427 nm ($\varepsilon = 6.1 \times 10^4$ L mol^{-1} cm^{-1}). The photoluminescence spectrum displays clear vibronic structures with peaks at 449 and 469 nm. These spectral features are similar to those of 1,6-bis(phenylethynyl)pyrene derivatives in the monomeric state.[29,30] Because cyclophane mechanophore **1** has two fluorophores, the molar extinction coefficient is larger than that of **2** (Fig. 2a). The absorption band in the range of 350–450 nm displays two peaks at 407 nm ($\varepsilon = 1.1 \times 10^5$ L mol^{-1} cm^{-1}) and 427 nm ($\varepsilon = 9.3 \times 10^4$ L mol^{-1} cm^{-1}). The fact that the spectral shapes of the absorption bands of **1** and **2** differ from each other suggested that intramolecular interactions between the two fluorophores of **1** occur in the ground state. The photoluminescence spectrum of **1** in DMSO exhibits a broad and structureless emission band with a peak at 530 nm (Fig. 2b), which is characteristic of the excimer emission of 1,6-bis(phenylethynyl)pyrene.[30] Because the spectral features remained unchanged at lower concentrations (Fig. S1, ESI†), the excimers intramolecularly form in the isolated compound **1**. The DMSO solution of **3** exhibits absorption and emission spectra almost identical to those of cyclophane mechanophore **1** in DMSO.

Fluorescence lifetime measurements for DMSO solutions of **1**–**3** ($c = 1.0 \times 10^{-6}$ M) were conducted to clarify intramolecular excimer formation (Fig. S2, ESI†). The fluorescence decay curve of **2** was fitted with a single exponential decay function, resulting in a monomer lifetime of 1.4 ns. In contrast, the slow decay curve recorded for **1** in DMSO was fitted with a tri-exponential decay function, and a longer lifetime of 31 ns was calculated, which is ascribed to excimer emission. The emission decay profile recorded for **3** is similar to that of **1**. The fluorescence quantum yields of compounds **1**, **2**,
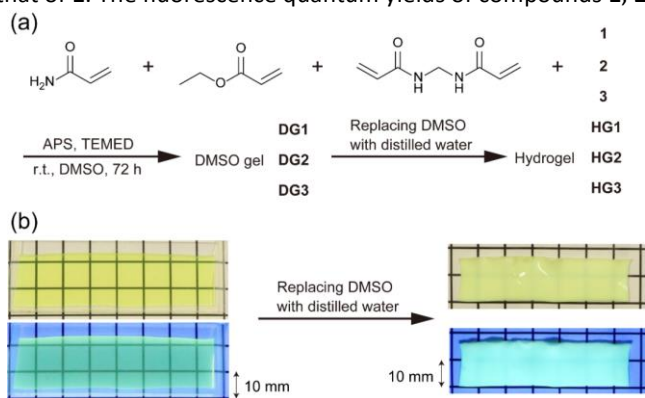
and **3** in DMSO solutions are 0.65, 0.85, and 0.77, respectively (Table S1, ESI†). These photophysical properties are similar to those of reported "parent" compounds **4** and **7** (see the ESI† for details).[19]

Next, compound **1**, **2**, or **3** was covalently introduced into hydrogels that were prepared through free radical polymerisation between acrylamide, ethyl acrylate (EA), and N,N'-methylenebisacrylamide (Fig. 3a, ESI†). Compounds **1** and **2** function as crosslinkers, whereas compound **3** does not cross-link the polymer chains. Therefore, the mechanical stress applied to the gels is transduced to the cyclophane part of **1**, whereas the cyclic part of **3** was not expected to be stretched. After free radical polymerization in DMSO, solvents in resultant DMSO gels (**DG1**, **DG2**, and **DG3**) were replaced with distilled water, resulting in the formation of corresponding hydrogels (**HG1**, **HG2**, and **HG3**). Reference gels **DG4** and **HG4** were prepared in the absence of compounds **1**–**3**.

After replacing DMSO in **DG1**–**4** with water, the gels shrank, and the thickness of resultant **HG1**–**4** decreased from 1.00 mm to ca. 0.70 mm. **DG1**–**4** were transparent; however, **HG1**–**4** were opaque (Fig. 3b), indicating phase separation between the hydrophilic and hydrophobic parts in the hydrogels. Similar phase-separated gels have been reported to exhibit high stretchability in the previous studies.[31,32] After removing water from **HG1**, **HG2**, and **HG3** in vacuum, dry polymers **DP1**, **DP2**, and **DP3** were obtained, respectively.

Small-angle neutron scattering (SANS) was performed on **HG1** to investigate the nanostructures inside the hydrogel. The nanostructures were confirmed to have a calculated radius of gyration R_g of 48 nm (Figs. 4 and S3, ESI†). To clarify whether the nanostructures are due to the self-assembly of the hydrophobic part mainly made from EA, ANS was used to detect the hydrophobic part. ANS generally exhibits strong emission in hydrophobic environments, while the emission intensity significantly decreases in water.[33] Gong and co-workers reported mechanochromic double-network hydrogels containing ANS.[5] Mechanical stimuli-induced cleavage of covalent bonds resulted in forming mechanoradicals, leading to polymerization of N-isopropylacrylamide. The resultant new chains self-assembled when the temperature was increased. ANS inside the gels visualized the hydrophobic self-assembly parts. In this study,
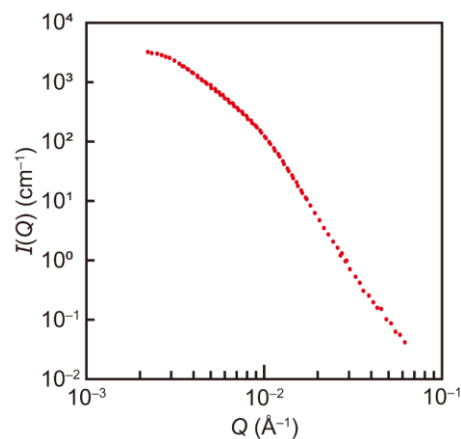

Fig. 3 (a) Preparation scheme of **DG1**, **DG2**, **DG3**, **HG1**, **HG2**, and **HG3**. (b) Pictures of **DG1** (top) and **HG1** (bottom) under ambient room light (left) and UV light at 365 nm (right).

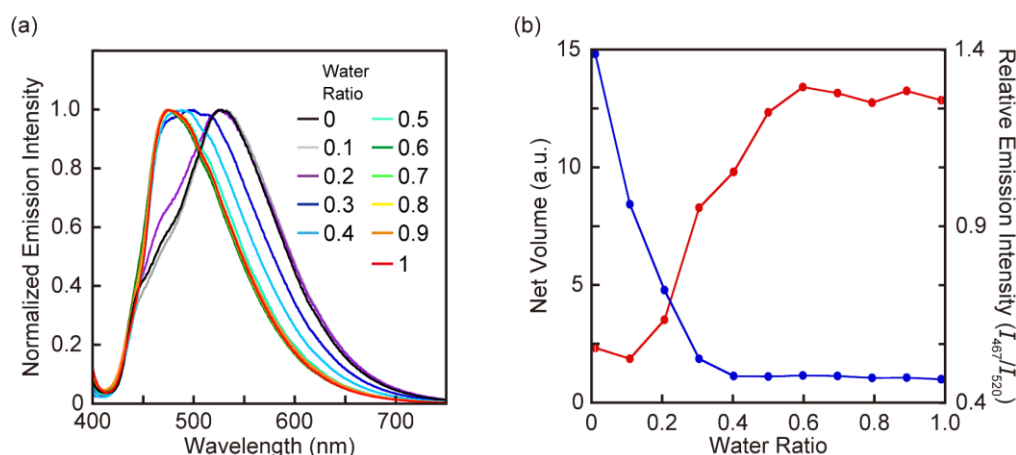

Fig. 4 SANS profile of **HG1**.

Fig. 5 (a) Fluorescence spectra of DMSO/water gels. The ratio of the mixed solvents varied by 10%. (b) Change of relative monomer to excimer intensity (red dots and line) and change of net volume with varying the proportion of DMSO/water in gels (blue dots and line). The excitation wavelength was 385 nm.

DG4 and polyacrylamide DMSO gel (see the ESI† for details), which does not have a hydrophobic part, were swollen with DMSO-containing ANS ($c = 1 \times 10^{-4}$ M), and thereafter, the solvents were replaced with water-dissolving ANS ($c = 1 \times 10^{-4}$ M). The quantum yield of the **HG4** containing ANS was ten times higher than that of the polyacrylamide hydrogel having ANS (Table S1, ESI†). These results indicate that phase separation between the hydrophilic and hydrophobic parts occurred after replacing DMSO inside the gels with water, resulting in gel shrinkage (Fig. 3b).

The mechanical properties of hydrogels **HG1–4** are shown in Figs. S4–8 and Table S2 (see the ESI† for details). All hydrogels exhibited excellent mechanical properties regardless of having fluorophores. The tough and stretchable properties of **HG1–4** were derived from phase separation.[31,32] When the hydrogels are deformed, the assembly of the hydrophobic part serves as a sacrificial bond to dissipate energy. This mechanism has also been adopted for other stretchable hydrogels.[34]

The photoluminescence properties of **DG1–3**, **HG1–3**, and **DP1–3** were examined in force-free states (Fig. S9, ESI†). The photoluminescence spectrum of **DG1** is excimer-dominant and exhibits a peak at approximately 530 nm. However, after replacing DMSO with water, the relative excimer emission

intensity decreases and the peak shifted to approximately 470 nm, corresponding to the emission colour change of the gel from green to cyan (Fig. 3b). To understand the spectral change further, **DP1** films were fully swollen in mixtures of water and DMSO with varying ratios, and the emission spectra and the net volume (see the ESI† for details) were measured (Fig. 5). As the water fraction increases from 10 to 50%, the emission spectrum exhibits a significant blue shift (Fig. 5a). When the water ratio is higher than 10% in the solvent mixture, the relative monomer to excimer intensity (I_{467}/I_{520}) increases (Fig. 5b). The I_{467}/I_{520} ratio becomes almost constant when the water ratio exceeds 50%. Simultaneously, the gel-shrinking effect ends. The net volume of the gel gradually decreases as the water ratio increases to 0.4 (Fig. 5b). These results indicate that most of cyclophane **1** are incorporated in the hydrophobic parts of the hydrogels when phase separation occurs upon increasing the water fraction in the solvent mixture. Suppression of mobility in the hydrophobic part in which the polymer density becomes significantly high and most solvent molecules are removed results in the kinetic trapping of the cyclophane mechanophores into arrangements where the luminophores cannot form excimers.[19] This is supported by the fact that the
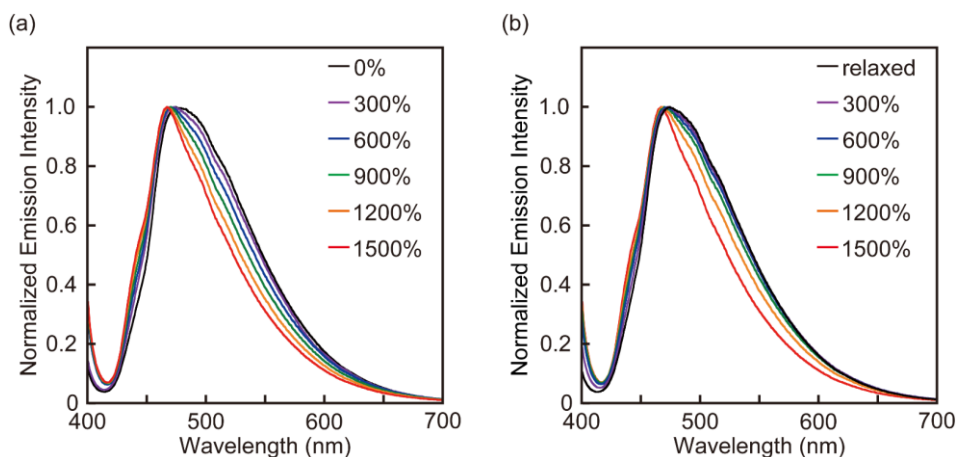

Fig. 6 Photoluminescence spectra of **HG1** recorded during a first (a) stretch and (b) release cycle at indicated strains. The excitation wavelength was 385 nm.
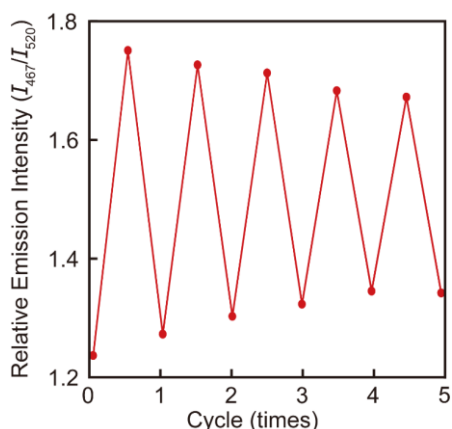
Fig. 7 Plot showing the ratio I_{467}/I_{520} in the stretched (1300% strain) and relaxed state of **HG1** recorded over 5 cycles. The excitation wavelength was 385 nm.

relative excimer intensity of **DP1** decreases further because more cyclophanes are kinetically trapped in the dry polymer films. Notably, the differences in the photophysical properties between **DG3** and **HG3** (Fig. S9c, ESI†) are similar to those observed between **DG1** and **HG1** (Fig. S9a, ESI†). This excludes the possibility that the phase separation process results in force transduction through the polymer network and activates the cyclophane mechanophores in **HG1**.

Finally, the mechanochromic luminescence of **HG1**, **HG2**, and **HG3** under deformation was investigated (Figs. 6, S10, and S11, ESI†). The relative excimer emission intensity of **HG1** gradually decreased during deformation (Fig. 6a) and the emission lifetimes became shorter (Fig. S12, ESI†). These changes indicate that the force macroscopically applied to **HG1** transduced to mechanophore **1** at crosslinking points via the polymer chain. When **HG1** was maintained at a stretching ratio of 1300%, the stress and the relative monomer to excimer intensity correlatedly decreased (Fig. S13 ESI†). After the applied force was released, the initial emission properties were recovered (Fig. 6b). In contrast, **HG2** did not exhibit a clear change in the emission spectra upon stretching (Fig. S10), confirming that cyclophane **1** functions as a mechanochromic mechanophore at the single-molecule level in the hydrogels. The change of the emission spectrum for **HG3** is smaller than that of **HG1** (Fig. S11, ESI†). This indicated that **HG1** can effectively detect the force applied to the polymer chain by introducing the mechanophores at the cross-linking points. Cycle tests confirmed the reversible mechanochromic photoluminescence properties of **HG1** over five cycles (Fig. 7). Notably, the I_{467}/I_{520} value in the force-free state gradually increases during the cycle test. Because the evaporation of water inside the gel was accelerated during deformation, the proportion of the hydrophobic part increased, resulting in enhanced monomer emission. Indeed, the swelling ratio after the cycle test decreased from 0.40 to 0.25.

Conclusions

In summary, mechanochromic luminescent hydrogels were developed by introducing cyclophane mechanophore **1** at the cross-linking points. Free radical polymerisation of a mixture of hydrophilic and hydrophobic monomers allowed us to access phase-separated, highly stretchable hydrogels that exhibit ratiometric changes in photoluminescence upon stretching. Most cyclophanes are included in the hydrophobic part of the hydrogels because of their hydrophobicity. The development of hydrophilic mechanophores is ongoing in our group. Such mechanophores would detect and visualize tiny forces that occur in meso-scale functional materials with hierarchical structures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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