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Supporting Information

Decoupling Dual-Stimuli Responses in Patterned Lamellar Hydrogels as Photonic Sensors

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Materials. Dodecyl glyceryl itaconate (DGI; n-$C_{12}H_{25}$-$OCOCH_2C(=CH_2)COOCH_2CH(OH)$-$CH_2OH$) was synthesized as the procedure described by Tsuji et al.[S1] The crude product was purified by a silica gel column and eluted with a hexane/ethyl acetate mixture (1:1 by volume). The collected DGI fraction was further purified by recrystallization from an acetone/hexane mixture (1/1 by weight). N,N′-methylenebis(acrylamide) (MBAA) was recrystallized from ethanol, acrylamide (AAm) was recrystallized from chloroform, Irgacure 2959, and sodium dodecyl sulfate (SDS) was used as received.

Reflection spectrum. Xe lamp was used for light source to obtain the reflection spectrum. Variable angle reflection measurement optics (Hamamatsu Photonics KK, C10027A10687) were used for radiating white light on the gel and resulting the reflected light. A photonic multi-channel analyzer (Hamamatsu Photonics KK, C10027) was used for analyzing the detected signal. The entire reflection spectrum was obtained by keeping both the incident (Bragg's angle) and reflection angles at 60°, and the wavelength at maximum, λ_{max}, was obtained from the reflection spectrum. Before measuring reflection spectra, the solvents were carefully removed from the PDGI/*h*-PAAm gel surface. The reflection spectra of the PDGI/*h*-PAAm gel at different compressive strains was measured by fixing the gel sample between two glass plates and the predetermined strain was achieved by placing some plastic thin film of desired thickness between the glass plates with gel.

Swelling ratio measurement. The swelling ratios of the gel parallel to the bilayers direction was measured from the ratio of both the length and width of the plate shape gel, denoting as L_{pH}/L_0 and W_{pH}/W_0, respectively. The swelling ratio perpendicular to the bilayer sheets was measured from the ratio of thickness (T_{pH}/T_0) of the gel at different pHs. The length of the gel at different swollen state was measured by a slide calipers and the thickness was measured by a tensile-compressive test machine (Tensilon RTC-1310A, Orientec Co.). To measure the thickness, the distance between load cell and the lower plate of the tensilon was calibrated to zero when the normal load started to be detected. The sample was then put into the lower plate and the load cell was approached to the sample until a load was detected. This distance between the load cell and the lower plate of tensilon gives the accurate thickness whereas the thickness of soft gel was difficult to measure accurately by any other scales.

pH measurement. Phosphate buffer solutions of different pH values were made by mixing 0.1M KH_2PO_4 (aq.) with different quantities of 0.1M HCl (aq.) or 0.1M NaOH (aq.) and their pHs were measured with a pH meter (ORION 5 STAR, Thermo Scientific). The hydrolyzed gels (PDGI/*h*-PAAm) were cut into desired shape and then immersed in different pHs solution for 2 days until the equilibrium state achieved. For a control experiment, the intact PDGI/PAAm gel was also immersed in various pH solutions.

Scanning Electron Microscopy (SEM) characterization. SEM was used to characterize the structures of the gels before and after hydrolysis. The samples were flash-frozen by dipping in liquid nitrogen to protect the structure, and then they were split into small pieces. The sample pieces were quickly transferred to a free-dryer for two days to remove the water. The cross-section of the samples were detected by a JSM-6010LA SEM machine.

Mechanical characterization. The compression test was performed on the gels in the direction normal to the layers. The compressive velocity was maintained as 0.5 mm/s. The Young's modulus of the samples wascalculated from the initial slope of the compressive stress-strain curves within 8% strain change.

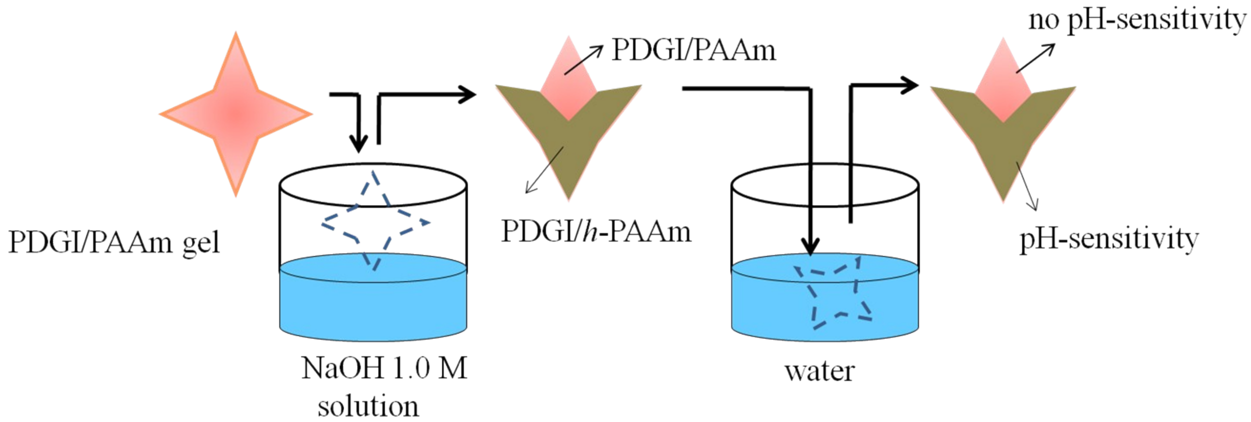

Figure S1. Schematic illustration of selective hydrolysis of PDGI/PAAm gel into a patterned gel. The bottom part of the PDGI/PAAm gel was immersed in hot 1.0 M NaOH solution while the top part was exposed in the air. Then, the concentrated NaOH solution diffused into the bottom part of the gel. Several minutes later, the gel was immersed in waterfor several days. The top part of PDGI/PAAm showed no pH sensitivity while the bottom part of PDGI/*h*-PAAm shows pH-sensitivity.

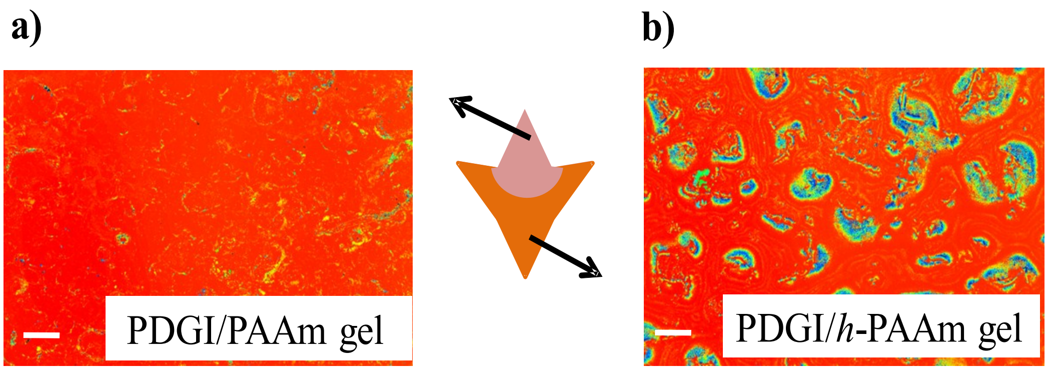

Figure S2. Surface morphology of the PDGI/PAAm and PDGI/*h*-PAAm gel. Compared with the virgin gel, the hydrolyzed gel has many cavities that aid inthe rapid uptake and loss of the fluids into/out of the gel, which improves the response time. Scale bar in a, b : 1μm. The samples were observed using a color 3-D violet laser scanning microscope (VK-9700, KEYENCE Co., Ltd.).

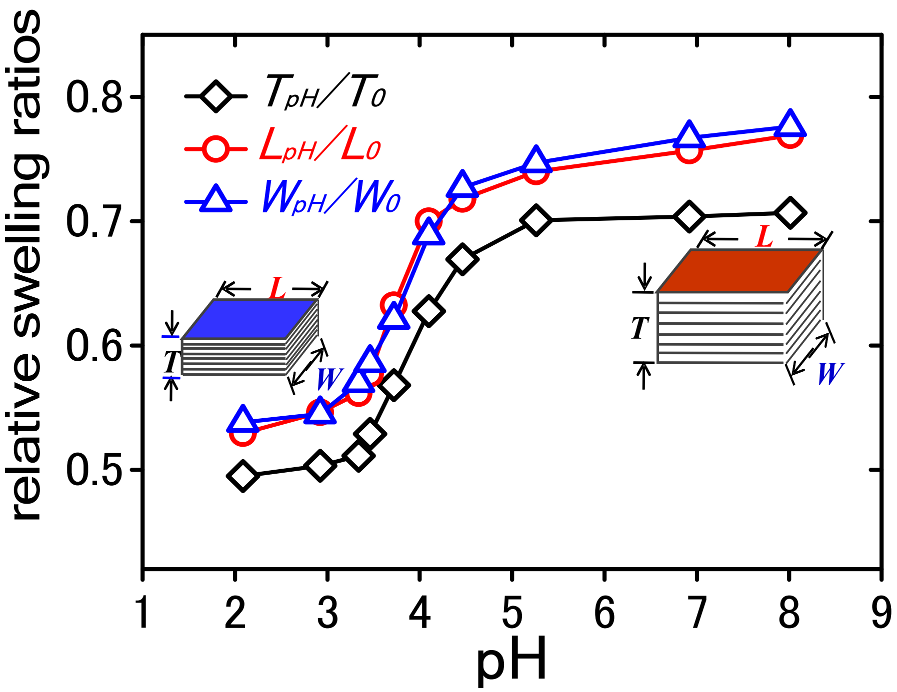

Figure S3. **Swelling behaviour.** Relative swelling ratios of PDGI/h-PAAm gel in different pHs along the thickness axis (perpendicular to the bilayers, T_{pH}/T_0), along the length axis (parallel to the bilayers L_{pH}/L_0) and along the width axis (parallel to the bilayers W_{pH}/W_0). The subscripts, '0' refers to the dimension of PDGI/h-PAAm gel at water swollen state and 'pH' refers to the dimension of PDGI/h-PAAm gel at an equilibrium state in pHs (ionic strength=0.1 M).These photonic hydrogels are usually keep in water-swollen states. Thus here we use the water swollen state as a reference, which will not affect the trend of swelling behaviour in pHs.

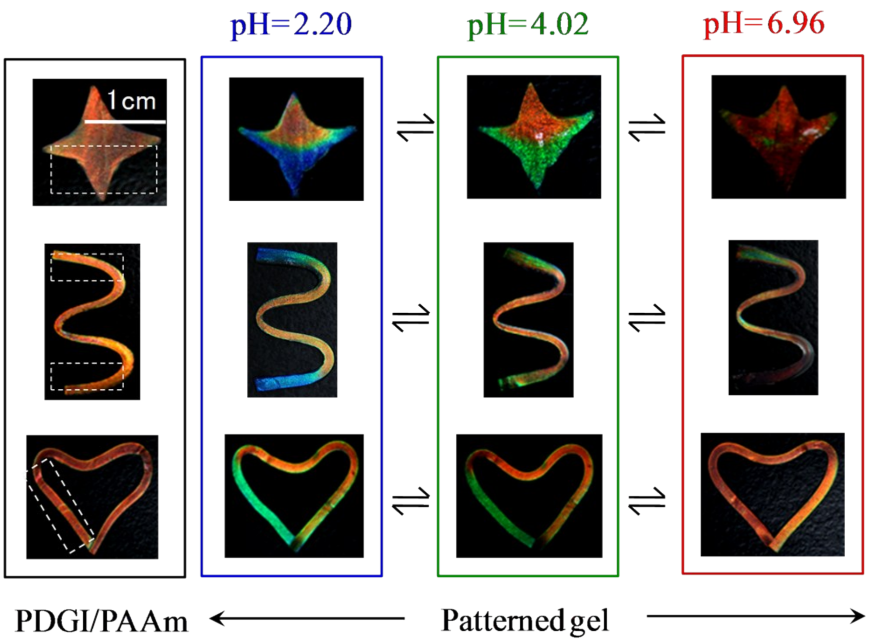

Figure S4. Photographs of patterned photonic hydrogels with local pH selectivity. The left column is the virgin 1-D photonic PDGI/PAAm gels of various shapes in water (upper: star-shape, middle: 'M' shape, and lower: heart-shape). These gels were used for selective hydrolysis in the regions surrounded by the white dotted lines. The right three columns are these gels after selective hydrolysis and being swollen in different pH solutions (pH= 2.20, pH= 4.02 and pH= 6.96). The hydrolysed regions change color from orange to green to blue with the decrease of pH while the non-hydrolysed regions do not change color.

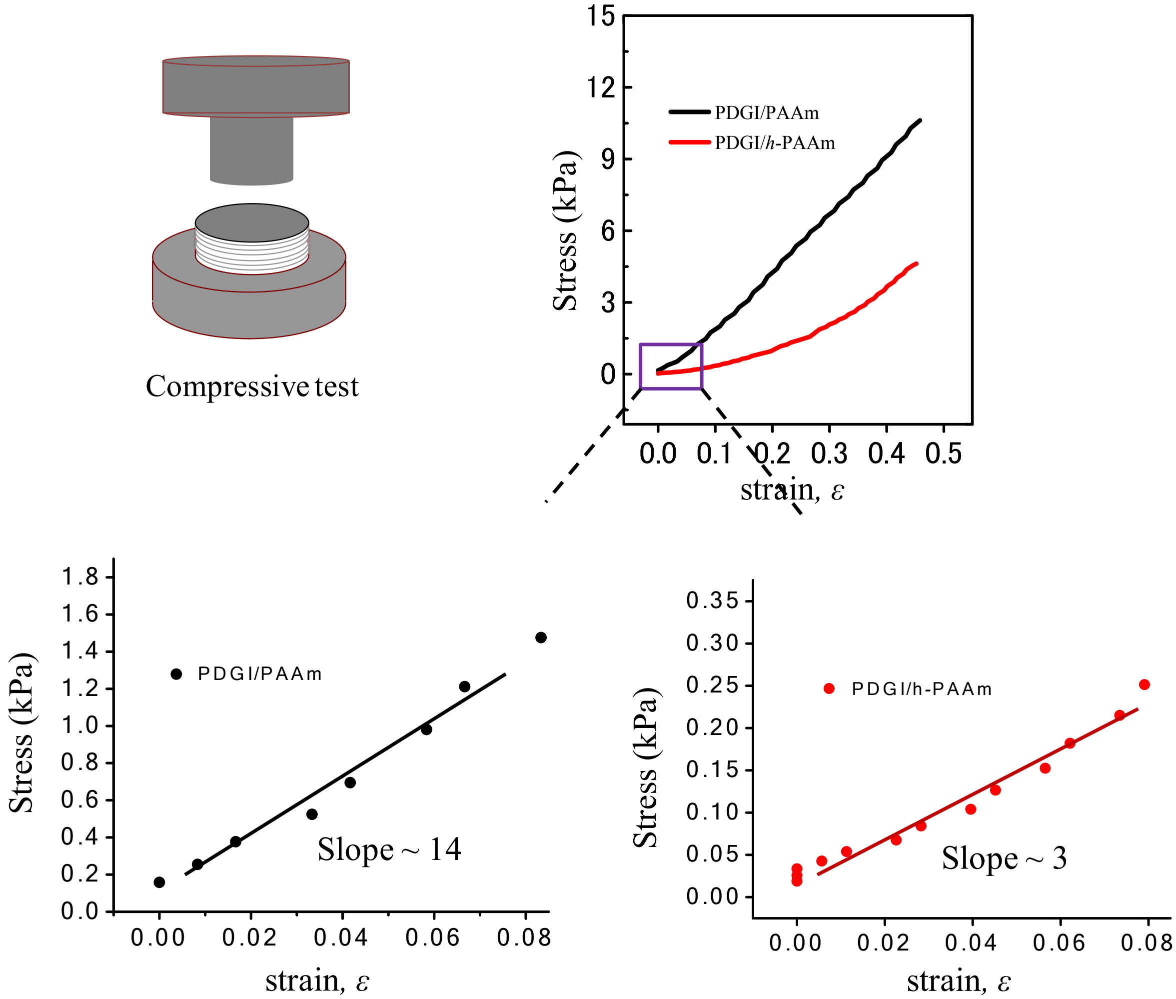

Figure S5. Different mechanical properties of PDGI/PAAmand PDGI/h-PAAm gel. The Young's modulus of PDGI/PAAm gel (~14 kPa) is much higher than that of the PDGI/h-PAAm gel in pH=6.9 (~3kPa), resulting in two stress sensors with different sensibility and measuring ranges. The compressive velocity was maintained as 0.5 mm/s.

[S1] Tsujii, K.; Hayakawa, M.; Onda, T.; Tanaka, T. *Macromolecules* **1997**, *30*, 7397.