Supplementary Information

for

Photo-responsive gel droplet as a nano- or pico-liter container comprising a supramolecular hydrogel

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Experimental Section

Preparation of gel droplets: 1.0-0.1 μL of gel droplets were prepared by adding heat-dispersed sol of hydrogelator **1** to hexadecane via micro-pipette injection. For the preparation of less than 0.1 μL of gel droplets, immediately after 2 μL of the heat-dispersed sol of **1** was added dropwised to 2 mL hexadecane, the solution was agitated via Vortex mixing. This solution was transferred to a glass-bottom dish and then we observed gel droplets thus prepared with a confocal laser scanning microscope (CLSM, OLYMPUS, FV1000). [Hydrogelator **1**] = 0.1 wt% (ion-exchanged-water).

Observation for Brownian motions of micro-beads in gel droplet: The heat-dispersed sol of **1** in ion-exchanged water containing 250 nm-fluorescent beads (micromer®-red F, POL) were dropped to hexadecane on a glass-bottom dish and left for 30 min at room temperature. These samples were monitored with a confocal laser scanning microscope (CLSM, OLYMPUS; FV1000) in real time. [Hydrogel **1**] = 0.1 wt% (ion-exchanged water).

Regulations for dye transfers and enzymatic reactions by photo-responsive fusion-capable gel droplets: 0.5 μL of heat-dispersed sol of **1** (0.125 wt%, 50 mM Tris-HCl buffer, pH 8.0) containing 50 μM Cy-5 (50 mM Tris-HCl buffer, pH 8.0) or 50 μM Fluorescein (50 mM Tris-HCl buffer, pH 8.0) was dropped into 1.5 mL hexadecane on a glass-bottom dish. In the same way, gel droplets without dye were prepared. These droplets were placed in contact with each other by lightly shaking the dish. In the experiment of UV irradiation, a low-pressure mercury vapor lamp (Ushio; UL0-6DQ) was located approximately 1 cm above the dish and UV-irradiation was conducted for less than 3 min. In enzymatic reactions, alkaline phosphatase (TOYOBO) and 3-*O*-Methylfluorescein phosphate cyclohexyl ammonium salt (SIGMA) as the substrate, or glucosidase (SIGMA) and 4-Methylumbelliferyl □-*D*-Glucopyranoside (Wako) as the substrate were separately entrapped in gel droplets in the same manner. [Alkaline phosphatase] = 0.21 x 10^{-3} units/droplet (0.5 μL), [3-*O*-Methylfluorescein phosphate cyclohexyl ammonium salt] = 0.11 mM, [Glucosidase] = 4.0 x 10^{-3} units/droplet (0.5 μL), [4-Methylumbelliferyl β-*D*-Glucopyranoside] = 0.60 mM, 50 mM Tris-HCl buffer (pH 8.0)

Supplementary Movie S1 *3D*-fluorescence imaging movie of hydrogel **1** droplet (ca. 0.06 nL) stained with hydrophobic rhodamine.

Supplementary Movie S2 The inner space imaging movie of the droplet during UV irradiation with a low-pressure mercury vapor lamp. .

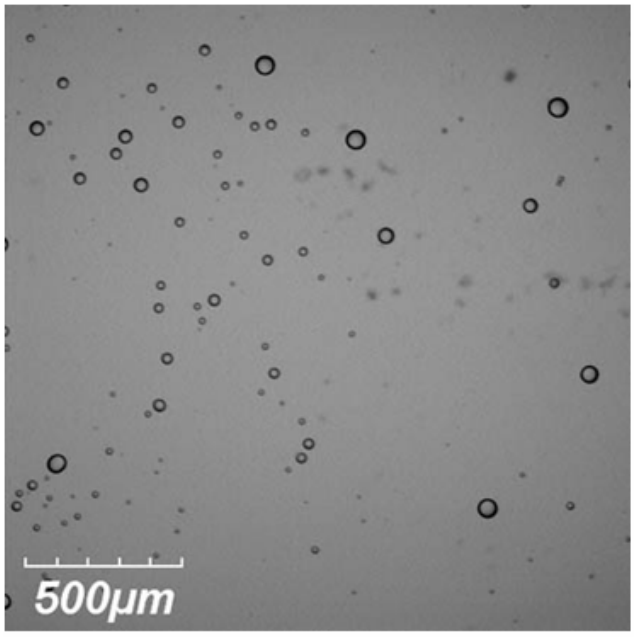

Figure S1
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Figure S1 Bright-field image of nL-volume gel droplets in hexadecane.

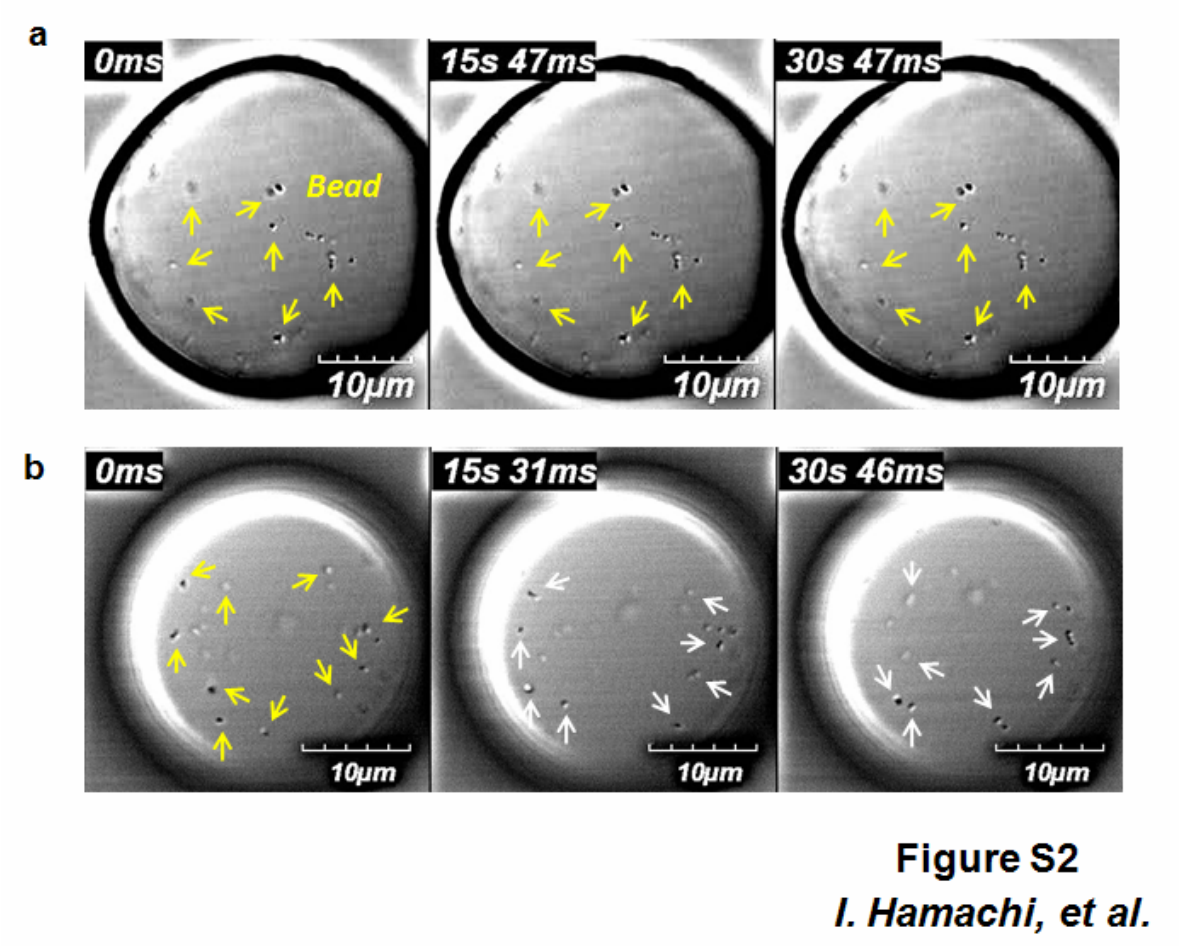

Figure S2 Time-dependent confocal laser scanning micrographs for the analysis of Brownian motion of hydrophilic 250 nm-beads **a**, in gel (**1**) droplet and **b**, in the sol droplet after UV irradiation with a low-pressure mercury vapor lamp for about 10 min.

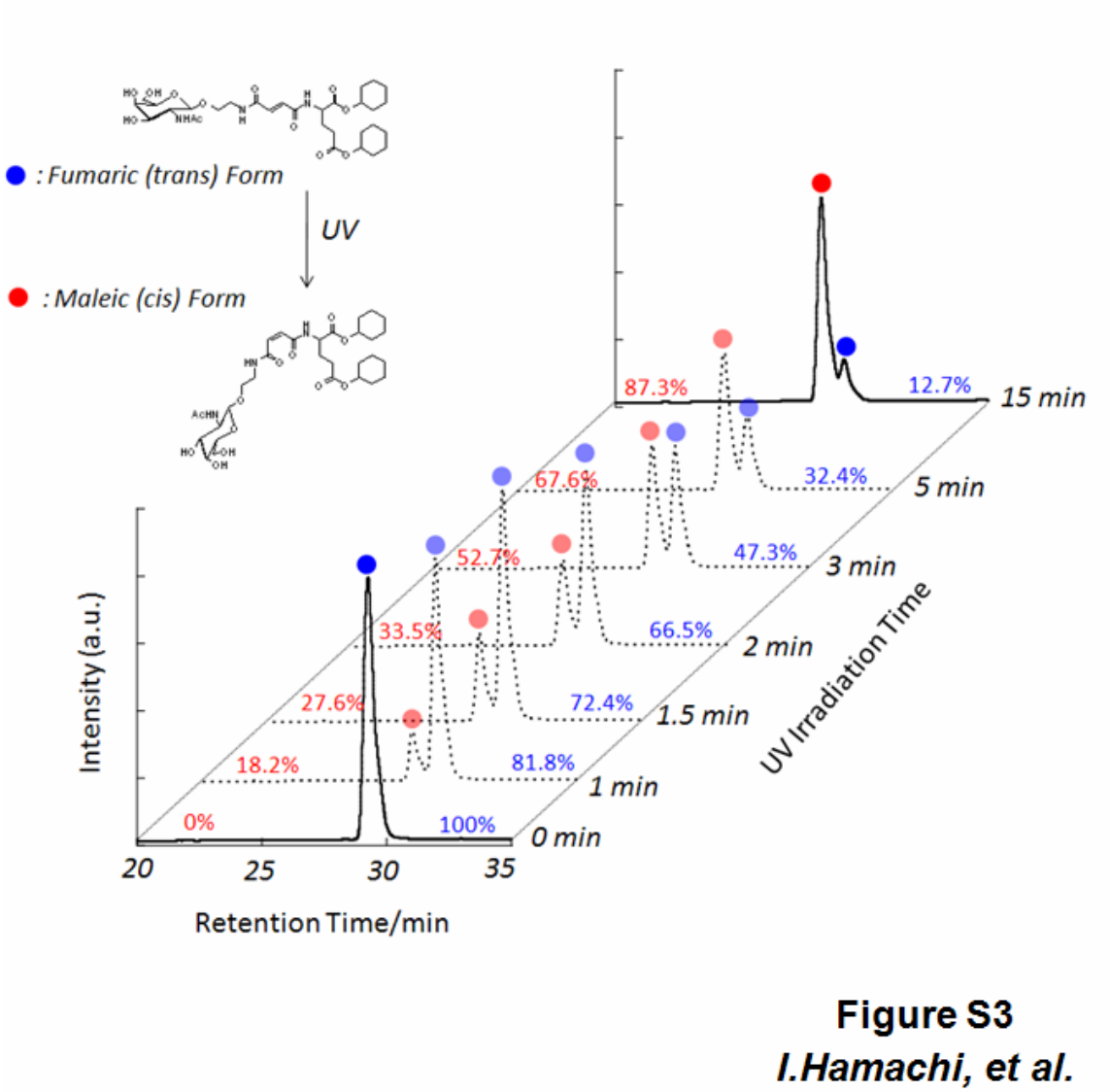

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Figure S3 HPLC analysis for photo-isomerization ratio of hydrogelator **1** in gel droplets ([**1**] = 0.125 wt%) by UV irradiation with a low-pressure mercury vapor lamp (0, 1, 1.5, 2, 3, 5 or 15 min). HPLC conditions are as follows: column, YMC-pack ODS-A, 4.6 Φ x 250 mm; mobile phase, CH_3CN (0.1% TFA)/H_2O (0.1% TFA) = 20/80-70/30 (linear gradient over 60 min); flow rate, 1.0 mL/min; detection, UV (204 nm, at isosbestic point before and after UV irradiation to **1**).

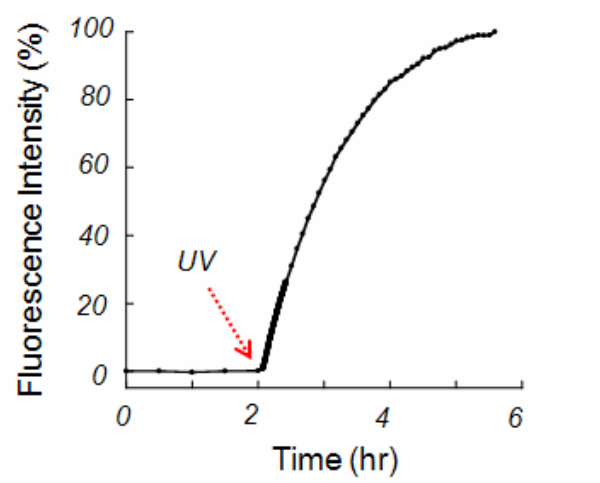

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Figure S4 Controlling of enzymatic reaction for glucosidase (GD) to 4-methylumbelliferyl β-D-glucopyranoside (MUG, substrate of GD) with photo-fused hydrogel droplets (**1**). Time course of fluorescence intensity of the reacted fluorescent substrate in the GD containing droplet was monitored with CLSM at excitation wavelength of 351 nm. Red arrow showed the UV irradiation time for approximately 4 min with a low-pressure mercury vapor lamp.

References

S1. (a) Kiyonaka, S.; Zhou, S. L.; Hamachi, I. *Supramol. Chem.* **2003**, *15*, 521. (b) Kiyonaka, S.; Shinkai, S.; Hamachi, I. *Chem. Eur. J.* **2003**, *9*, 976.