Supporting Information

Experimental

Materials. *N,N*-dimethylacrylamide (DMAAm) and 1H,1H,5H-octafluoropentylacrylate (OFPA) were purchased from Fujifilm Wako Pure Chemical Industries (Osaka, Japan) and Tokyo Chemical Industries (Tokyo, Japan), respectively. The monomers were purified by passing them through an alumina column. *N*-(3-aminopropyl)methacrylate hydrochloride (NAPMAm) was purchased from Polyscience (Warrington, PA, USA) and used as received. The ATRP initiator, 2-bromoisobutyrate *N*-hydroxysuccinimide ester (BiB-NHS), was synthesised according to a previous paper.[1,2] Trichloro(octadecyl)silane was purchased from Sigma-Aldrich (St. Louis, MO) and used as received. The PFQNM-LC-A-CAL tips were purchased from Bruker (Billerica, MA, USA). All other reagents were purchased from Fujifilm Wako Pure Chemical Industries and used as received.

Preparation of NG gel. DMAAm (3.88 mL, 37.6 mmol), NAPMAm (357 mg, 2.00 mmol), *N,N'*-methylenebis(acrylamide) (MBAAm) (61.7 mg, 0.40 mmol) and *N,N,N',N'*-tetramethylethylenediamine (60 µL, 0.40 mmol) were dissolved in water (18 mL). The solution was cooled in an ice bath and degassed with argon. Then, a solution of ammonium persulfate (91.3 mg, 0.40 mmol) in water (2 mL) was added to the degassed solution, and the mixture was placed into a glass mold of 65 mm × 45 mm × 2 mm. The mold was maintained overnight at 4 °C. After gelation, the observed hydrogel was cut into the desired size and dialysed with water for more than 4 days.

Preparation of IG gel. NG gel was immersed in an aqueous solution of BiB-NHS (2.25 mM) with pyridine (3.3 vol%) and DMSO (3.3 vol%) for a short time (5 min). The unreacted ATRP initiator was removed by dialysis against water. The reaction scheme and the fabrication method of the IG gel is shown in Figs. S1a,b

Preparation of FG gel. POFPA-grafted chains were introduced to the IG gel by activators regenerated by electron transfer for atom transfer radical polymerisation (ARGET ATRP) in DMF solution at 22 °C for 16 h. ARGET ATRP was conducted at OFPA/$CuBr_2$/Me_6TREN/ascorbic acid = 2000/1/6/6, and the concentration of OFPA was adjusted to 1.25 M. The observed gel was dialysed against DMF to remove the unreacted monomer and was gradually replaced with water to prevent hydrogel from breakage. The reaction scheme and fabrication procedure of the FG gel is shown in Figs. S1c,d

FT-IR measurement. The attenuated total reflectance infrared radiation (ATR-IR) spectrum was recorded by IRSprit (Shimadzu, Co., Japan) with a diamond ATR accessory (GladiATR™, PIKE technologies, Inc., USA). Samples were prepared as swollen states of the gels and were scanned against an air background at wavenumbers ranging from 4000–400 cm^{-1} with a resolution of 4.0 cm^{-1}.

Confocal Raman microscopy measurements. Both FG and NG gels were analysed using a confocal Raman microscope (inVia Raman Microscope, Renishaw, UK), which was provided with a Raman spectrophotometre with a Leica TCS SP8 confocal platform. The excitation wavelength was 532 nm. The surface point (depth = 0 µm) was adjusted at the point of light reflection, which was detected by microscopy. The Raman spectra were then obtained for an exposure time of 60 s at ambient temperature and at depths of 1–1000 µm into the sample.

AFM measurement. NG gel and FG gel immobilised on glass slides were prepared for atomic force microscopy (AFM) measurements to prevent undesired movement of the sample during the measurement. The glass slide was treated with a UV-O_3 cleaner (UV253H, Filgen, Inc., Japan) for 15 min (28 $mW \cdot cm^{-2}$) and then a solution of 3-methacryloxypropyltrimethoxysilane (MPTMS, 1 v/v%) in toluene for 18 h. NG and FG gels were fabricated on the MPTMS-modified glass slides according to the aforementioned method. The surface morphology and mechanical properties of the hydrogels were characterised using an AFM (Bioscope Resolve system, Bruker, USA). The PeakForce QNM mode in fluid was chosen for the experiment operations with pre-calibrated hydrophilic tips (PFQNM-LC-A-CAL tips) (spring constant: 0.075–0.092 $N \cdot m^{-1}$, frequency: 45 kHz). Furthermore, hydrophobic tips were prepared by modifying the hydrophilic tips with octadecyl trichlorosilane using the following procedure. The PFQNM-LC-A-CAL tips were treated with a UV-O_3 cleaner for 15 min and placed in a separable flask. Then, 10 µL of octadecyl trichlorosilane and 1 mL of toluene (super dehydrated) was added under an argon atmosphere, and the silane coupling reaction was carried out at 150 °C for 18 h under reflux. Finally, the hydrophobized tips were washed with toluene and acetone and dried in a vacuum oven at 110 ˚C for 3 h. A 1 µm × 1 µm image was usually obtained at a scan rate of 0.5 Hz under

arbitrary operating conditions. The surface topography and other mechanical properties such as adhesion could be recorded simultaneously, and the root-mean-square roughness (Rq) of the specimens were analysed and directly calculated using AFM NanoScope Analysis software v1.8 (Bruker, USA). To obtain the Young's modulus of the hydrogels, the force volume mode was used to collect 16 force-distance curves (4 × 4 lines under 1 µm × 1 µm scan size) of each specimen under various preparation conditions. The histograms of adhesion force were formed from 65,536 (256 × 256) points of adhesion force in 1 µm × 1 µm (Fig.3 a,c,e,g) using AFM NanoScope Analysis software v1.8.

Transparency test. Images of the FG and NG gels were taken with a digital camera. The transmittances of each hydrogel were measured using a UV-Vis spectrophotometre (UV-2500, Shimadzu, Co., Japan).

Contact Angle measurements. To measure the contact angle of water and *n*-hexadecane on the hydrogel surfaces, a contact angle measuring system (DMs-301, Kyowa Interfaces Science, Co., Ltd., Souka, Japan) was used. On each sample surface, 2 µL of droplet was deposited in air for ten seconds after wiping out the surface. The contact angle was averaged from three different surfaces. The contact angle was measured 1 s after dropping and measured every 2 s after the first measurement (Fig. S5, S6(b)).

References

1 K. Matsukawa, T. Masuda, A. M. Akimoto and R. Yoshida, *Chem. Commun.*, 2016, **52**, 11064–11067.

2 K. Matsukawa, T. Masuda, Y. S. Kim, A. M. Akimoto and R. Yoshida, *Langmuir*, 2017, **33**, 13828–13833.

3 O. J. Chaudhary, E. P. Calius, J. V. Kennedy, M. Dickinson, T. Loho and J. Travas-Sejdic, *Eur. Polym. J.*, 2016, **84**, 13–21.

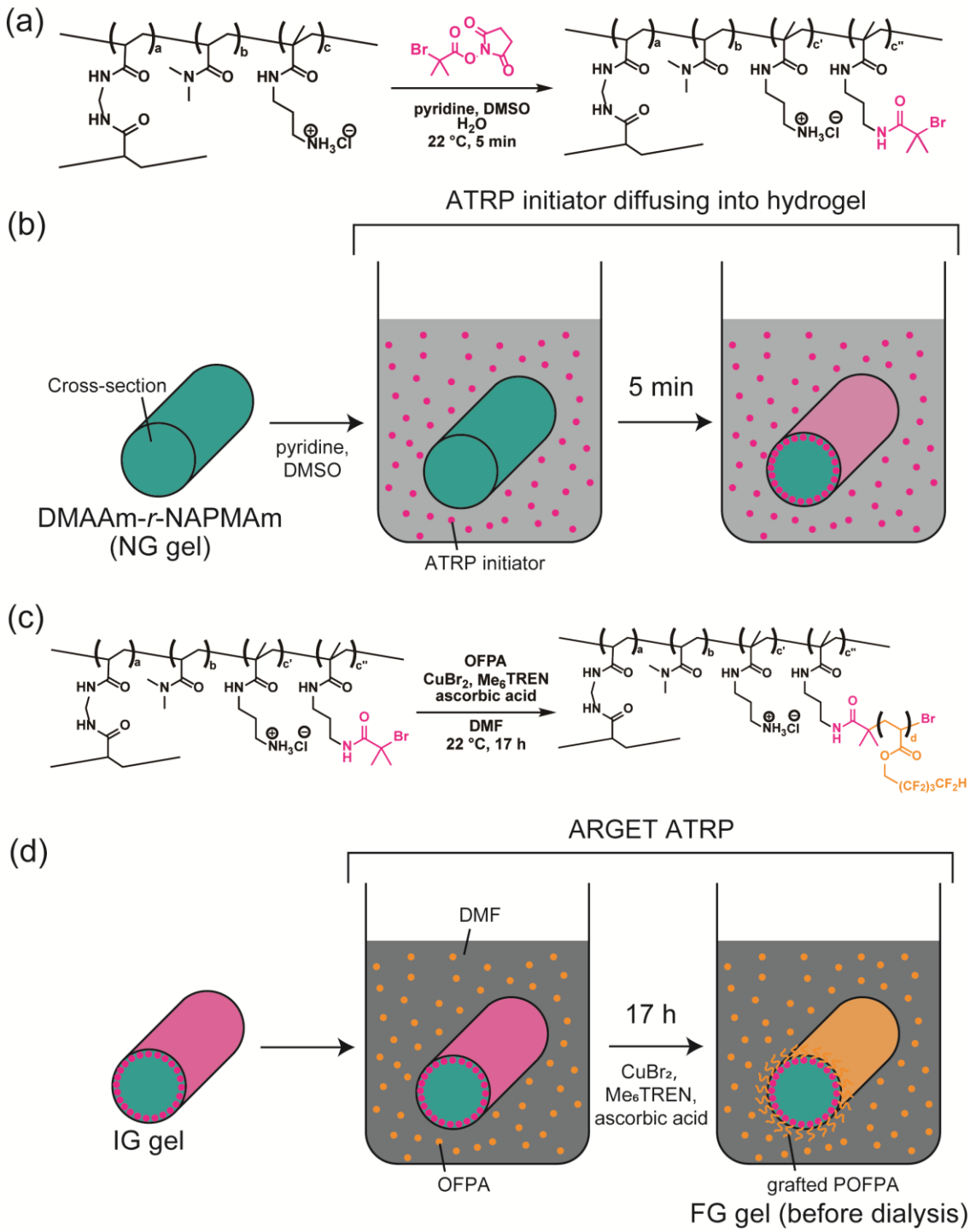

Fig. S1 Reaction schemes and schematic illustrations of the preparation of IG gel (a,b) and FG gel (c,d).

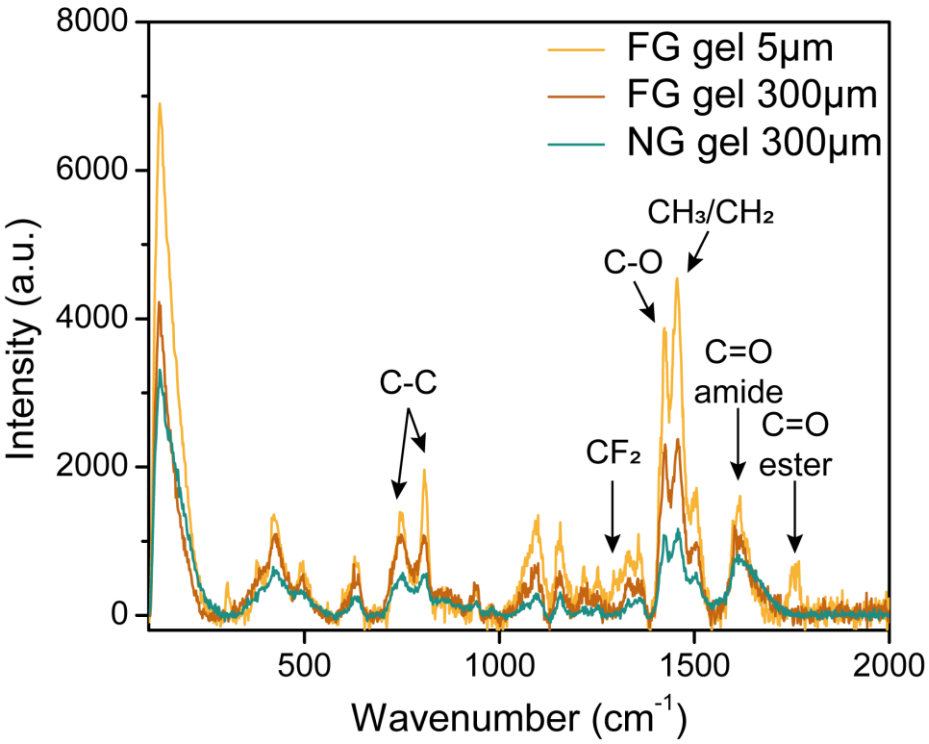

Fig. S2 Raman spectra of FG gel at 5 and 300 µm and NG gel at 300 µm in depth.

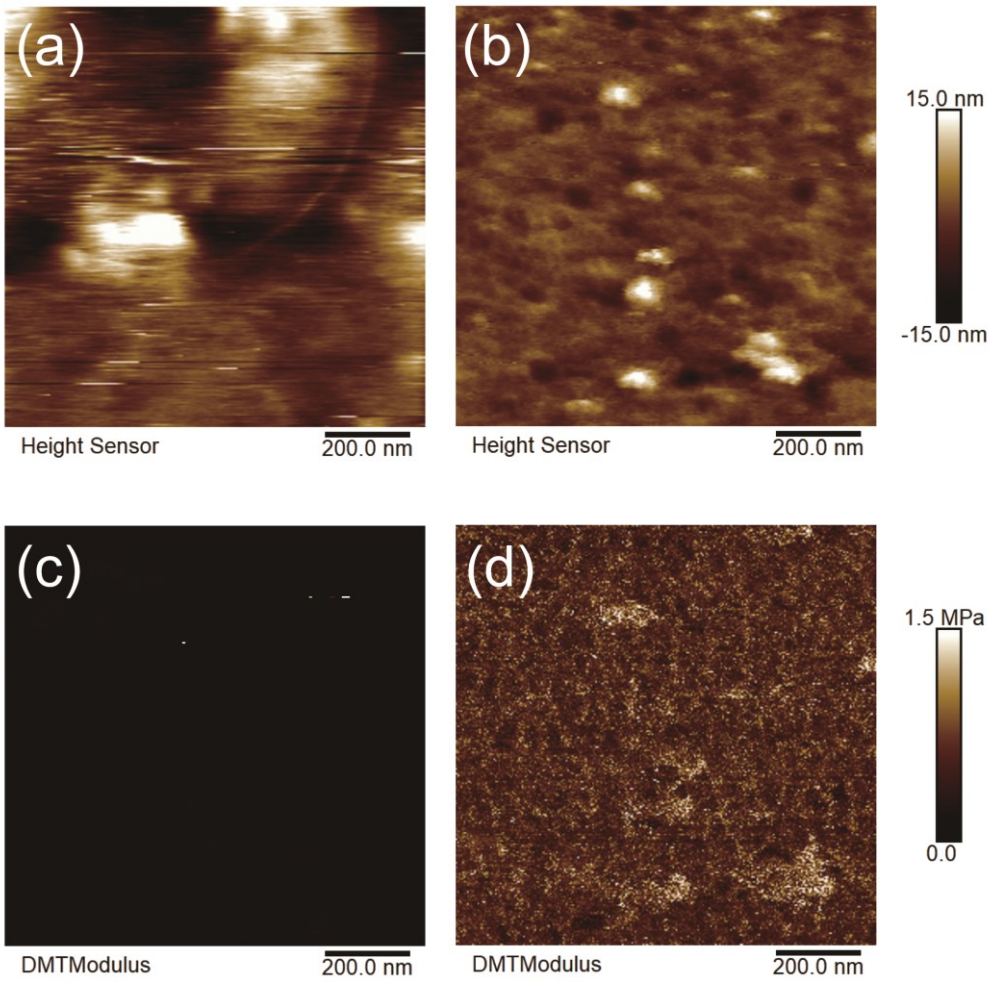

Fig. S3 Surface topography of (a) NG gel and (b) FG gel. Maps of elastic modulus of (c) NG gel and (d) FG gel using a hydrophilic tip.

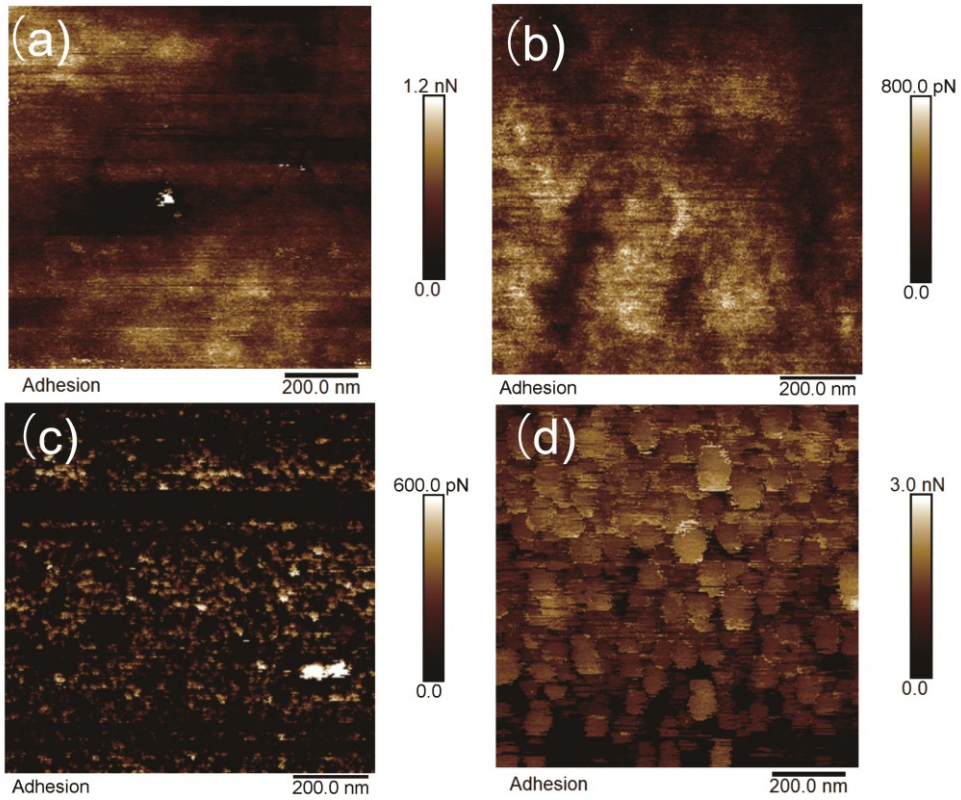

Fig. S4 Maps and histograms of adhesion force on NG gel with a hydrophilic tip (a,b) and a hydrophobic tip (c,d): FG gel with a hydrophilic tip (e,f) and a hydrophobic tip (g,h).

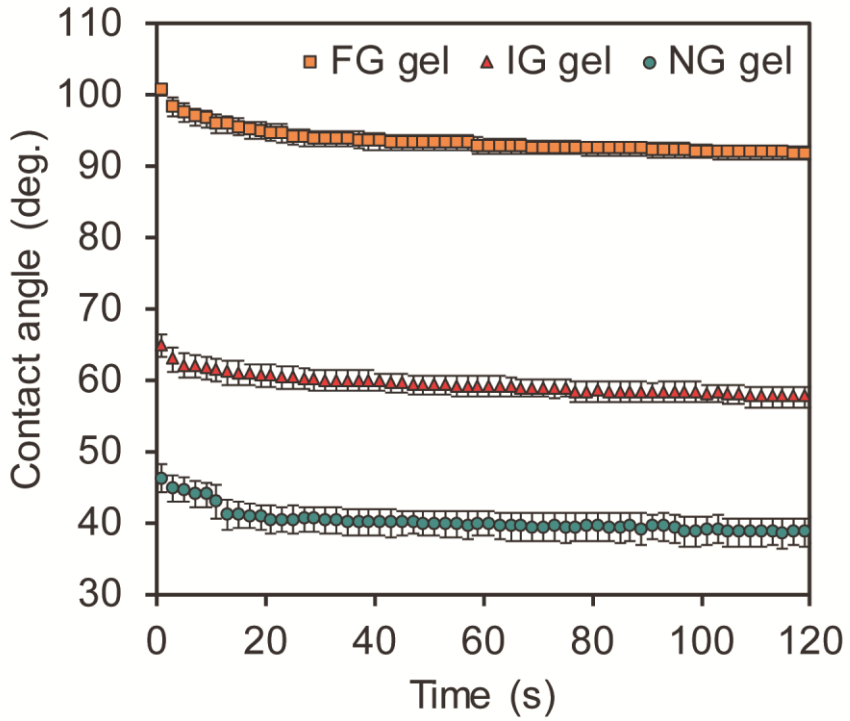

Fig. S5 Water contact angles on NG, IG, and FG gel with respect to time (n = 3).

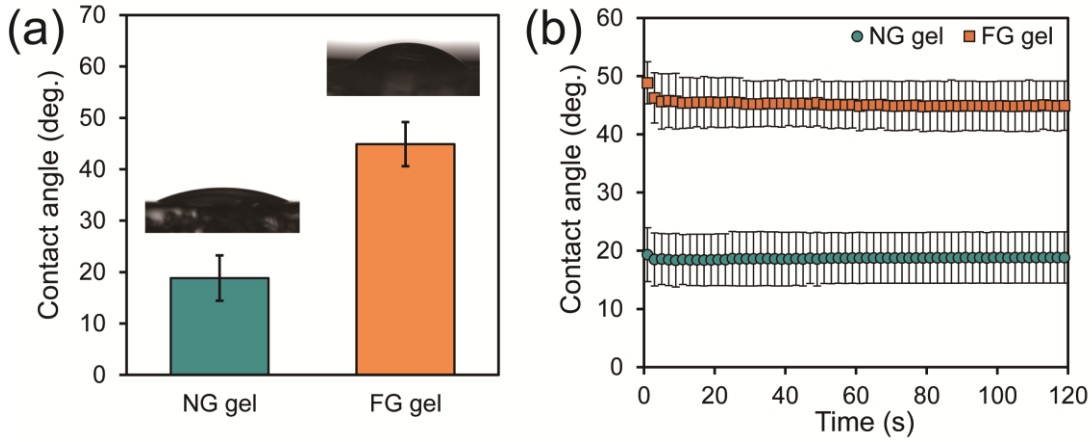

Fig. S6 (a)Images and contact angles of *n*-hexadecane deposited on NG and FG gel. (b) Contact angles of *n*-hexadecane on NG and FG gel with respect to time (n = 3)