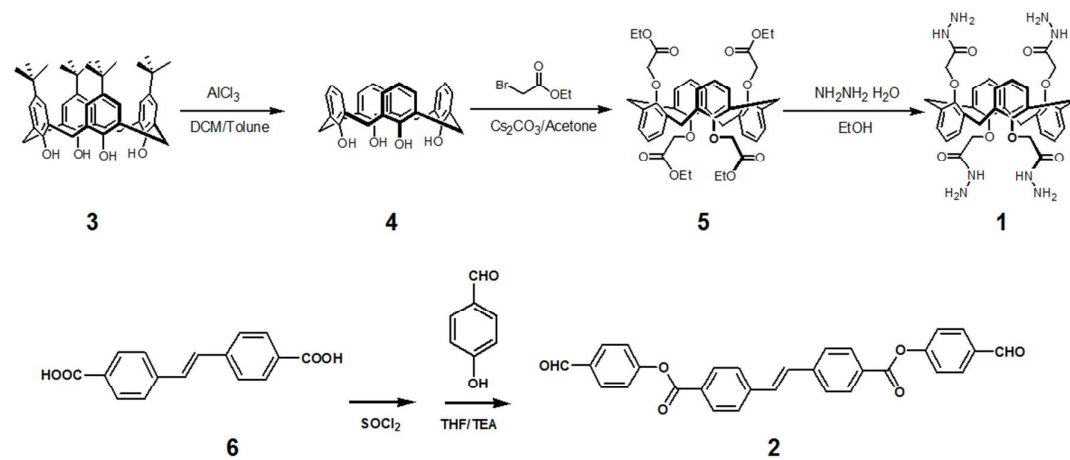


Supporting Information

Ultraviolet Patterned Calixarene-Derived Supramolecular Gels and Films with Spatially Resolved Mechanical and Fluorescent Properties

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Scheme S1. Schematic of synthetic methods for compounds **1** and **2**.



Figure S1. The photograph of gel formation of **1+2** (**1**: 42 mM and **2**: 42 mM) in the presence of HCl (5 nmol) by increasing hydrazone reaction times.

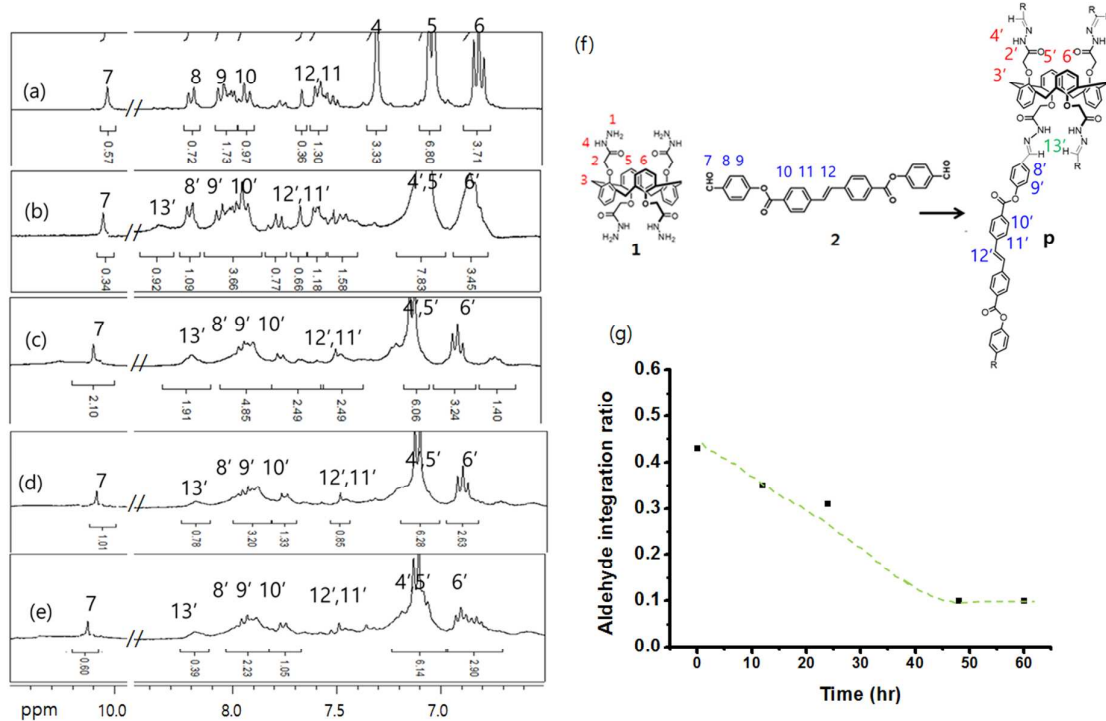


Figure S2. NMR spectra of gel (0.01M) (a) before and after adding HCl (5 nmol), (b) 12hr, (c) 24hr, (d) 48hr, (e) 60hr in DMSO- d_6 . (f) The plot of aldehyde integration ratio.

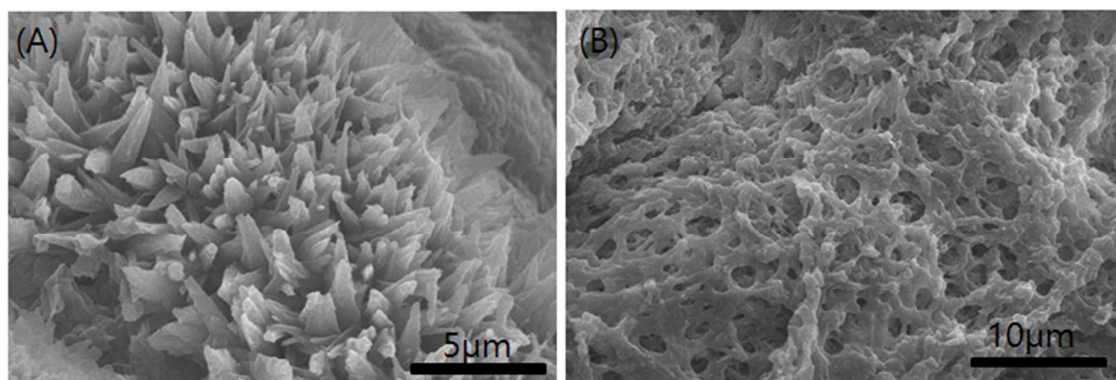


Figure S3. SEM images of gel obtained in acidic condition (a) before and (b) after UV irradiation (irradiation wavelength: 256 nm).

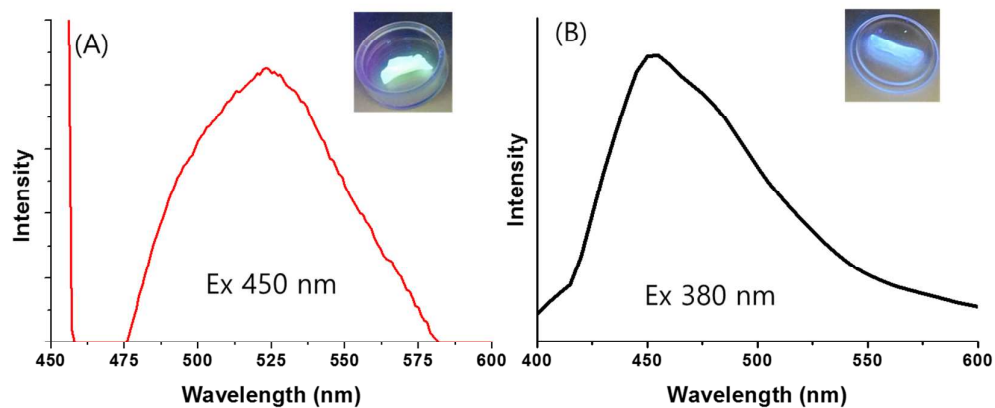


Figure S4. Fluorescence spectra of gel in acidic conditions; (A) after heating for 48hr (Ex: 450nm), and (B) after immersion in DMSO.

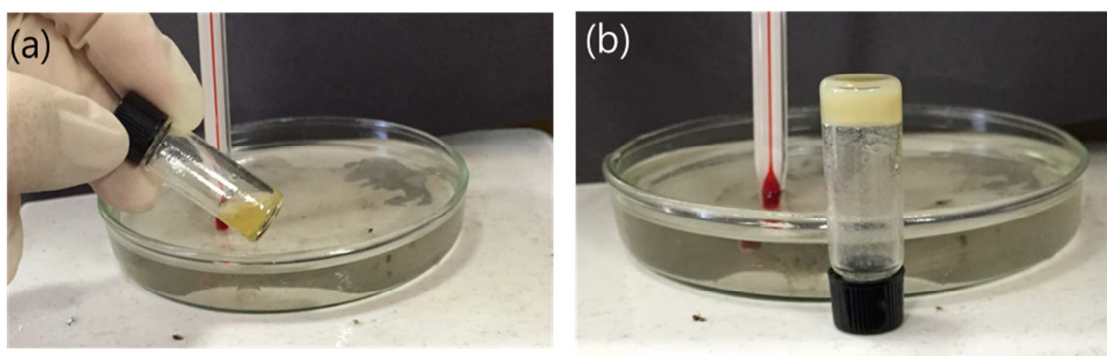


Figure S5. Photographs of the gel to sol transition (a) after and (b) before heating.

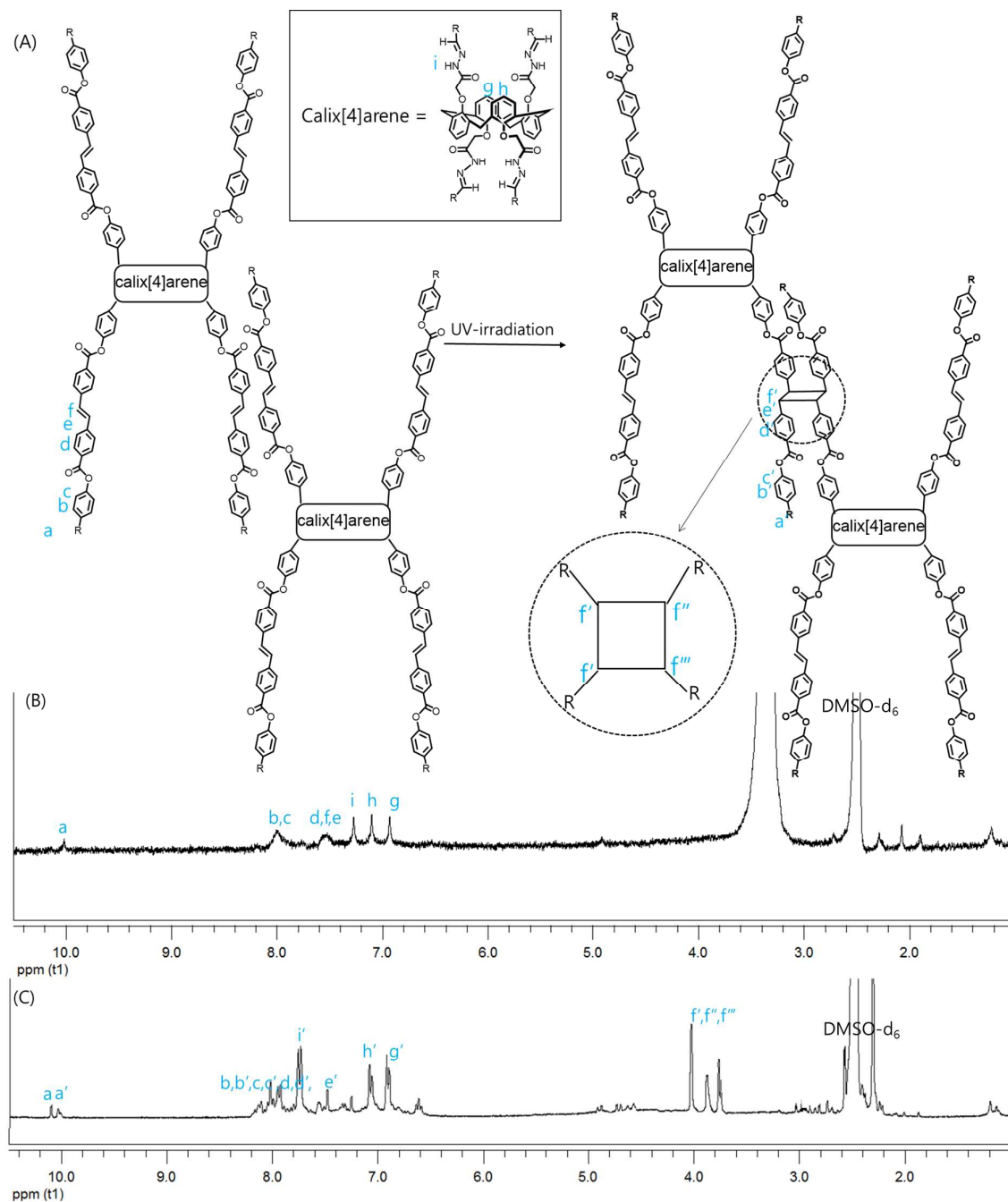


Figure S6. NMR spectra of gel (0.01M in DMSO- d_6) (A) before and (B) after UV irradiation (irradiation wavelength: 256 nm) wherein the “a” aldehyde peak exists for the un-photocyclized species and “a’” aldehyde peak exist in the photocyclized species. The f' , f'' , f''' peaks were due to different chemical environments after UV irradiation, because the various different chemical environments of the $-\text{CH}$ group of cyclobutane produced three distinct peaks of f' , f'' , f''' originating from the polymer. The additional aldehyde peak a' can also only be observed after UV irradiation as a result of the portion of photocyclized product.

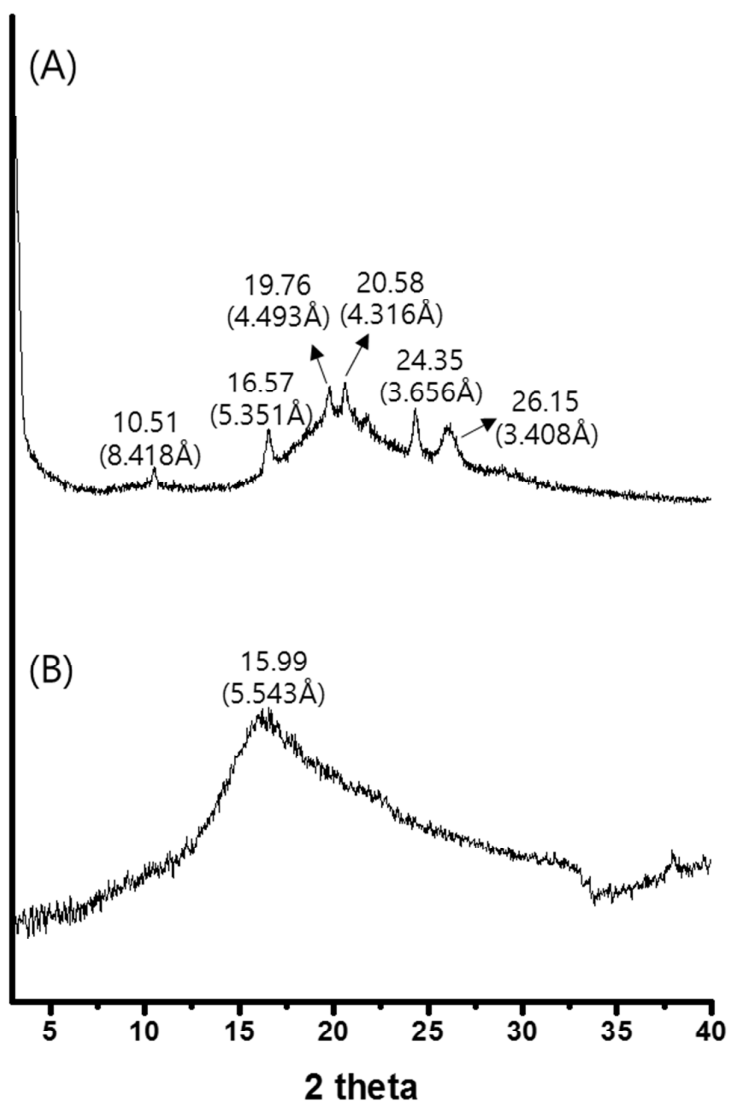


Figure S7. The X-ray powder diffraction (XRPD) patterns of gel obtained in acidic conditions (a) before and (b) after UV irradiation (irradiation wavelength: 256 nm).

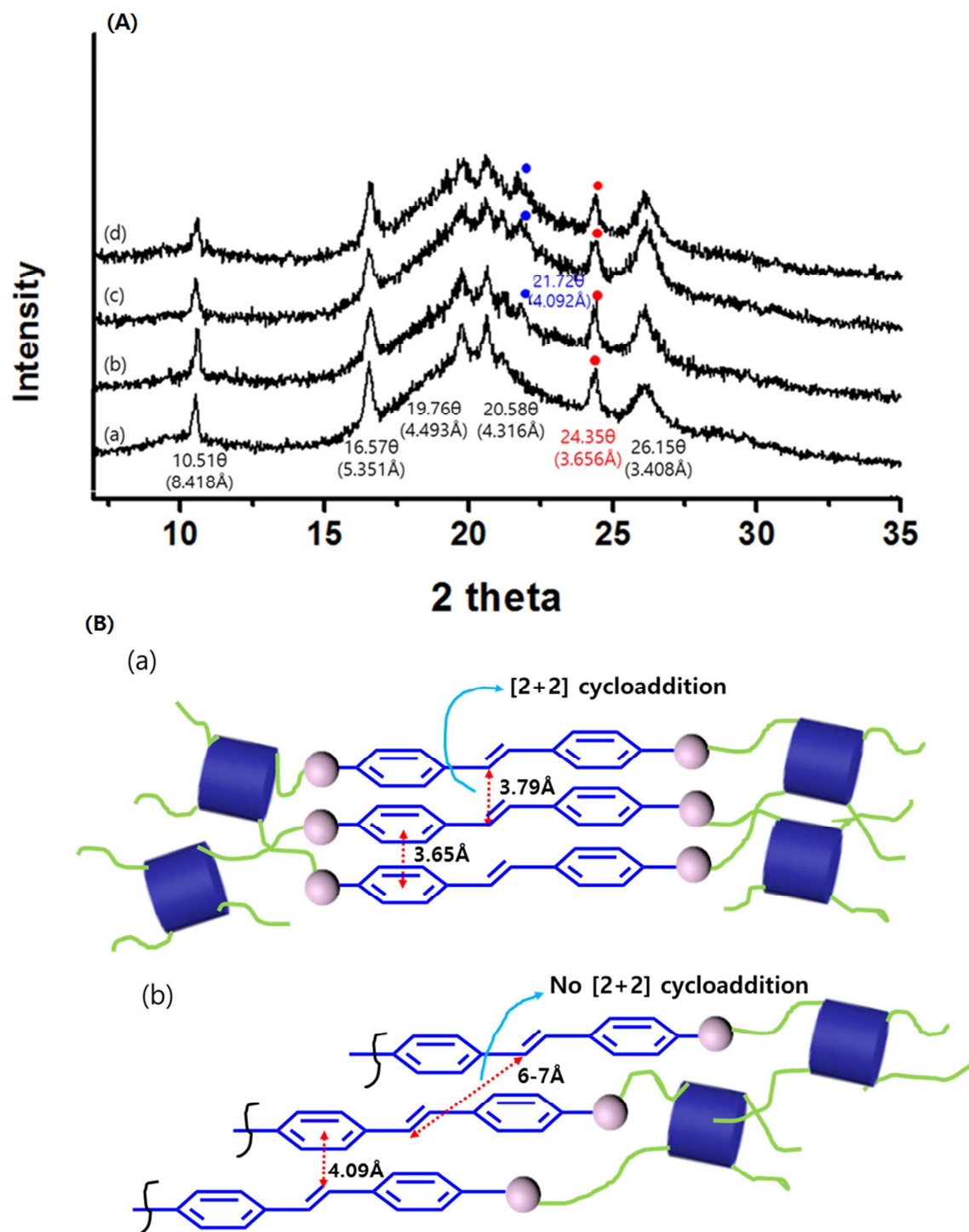


Figure S8. (A) X-ray powder diffraction (XRPD) patterns of gel obtained in acidic conditions after heating for 1 hr at (a) 30°C, (b) 40°C, (c) 60°C, and (d) 80°C. Schematic of (a) H aggregates and (b) J aggregates showing that the interlayer center-to-center distance of double-bonds in J-aggregates is too long for [2+2] cycloaddition to occur.

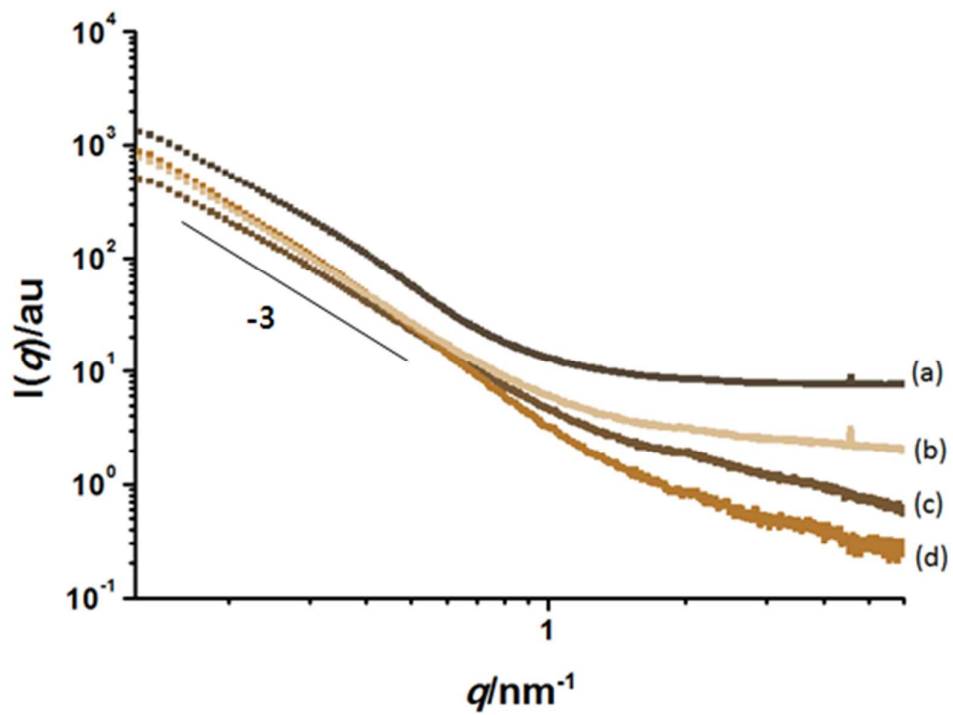


Figure S9. SAXS measurement of gel in acidic condition; (a) before UV irradiation of 0.5wt% gel, (b) before UV irradiation of 1.3 wt% gel (c) after UV irradiation of 0.5wt% gel and (d) after UV irradiation of 1.3 wt% gel.

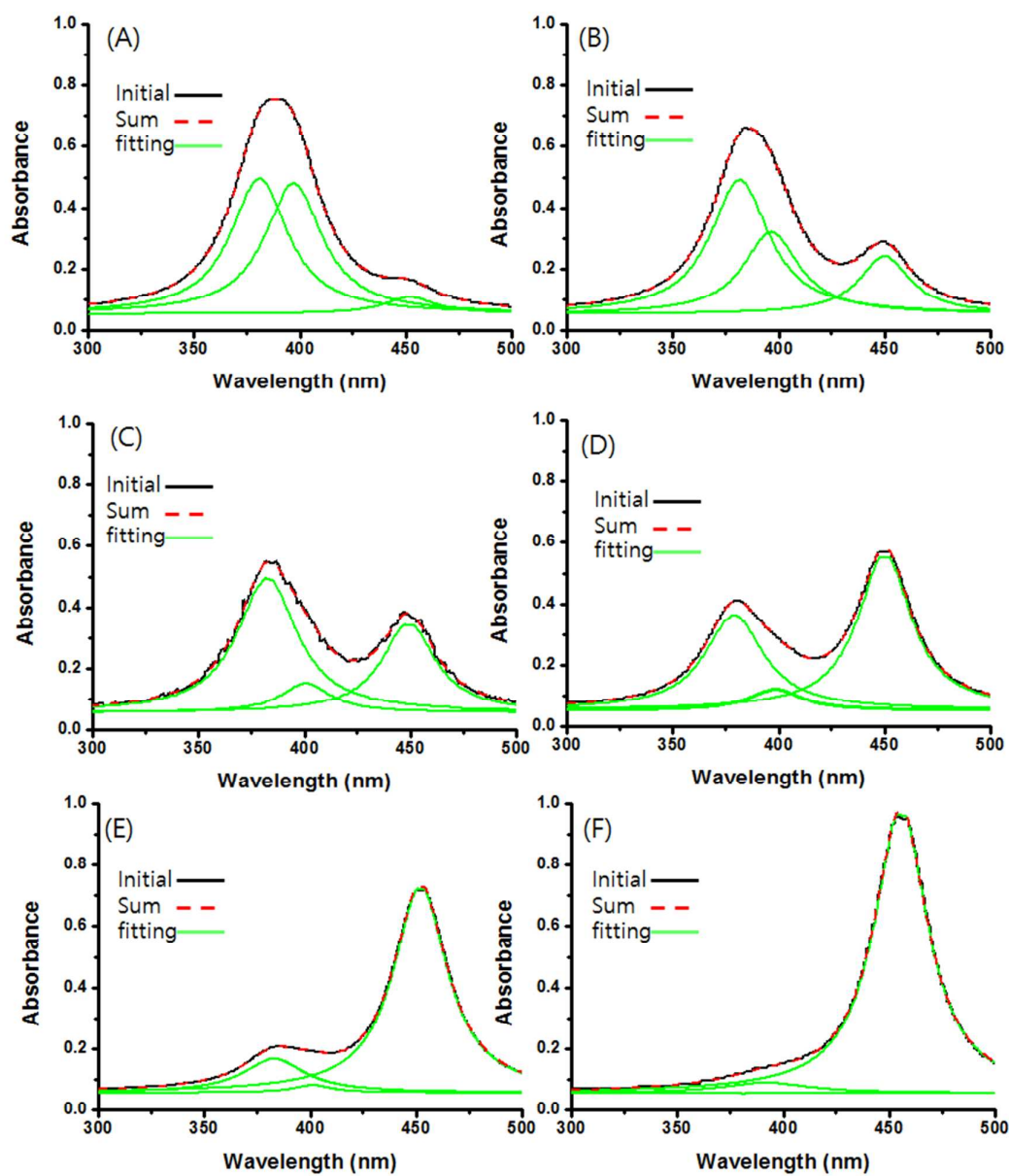


Figure S10. Fitting of UV spectra of gel obtained in acidic conditions (A) before and after heating for (B) 1hr, (C) 6hr, (D) 12hr, (E) 24hr, and (F) 48hr.

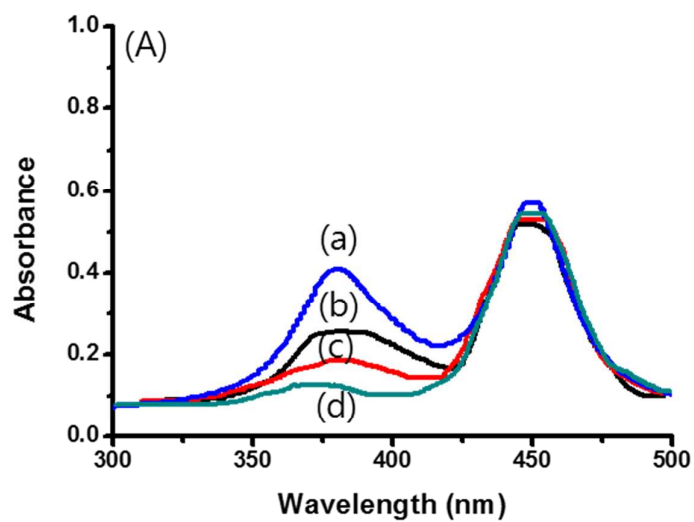


Figure S11. UV spectra of gel after heating for 12hr and then subjected to UV exposure for (a) 0 hr, (b) 12hr, (c) 24hr and (d) 48hr.

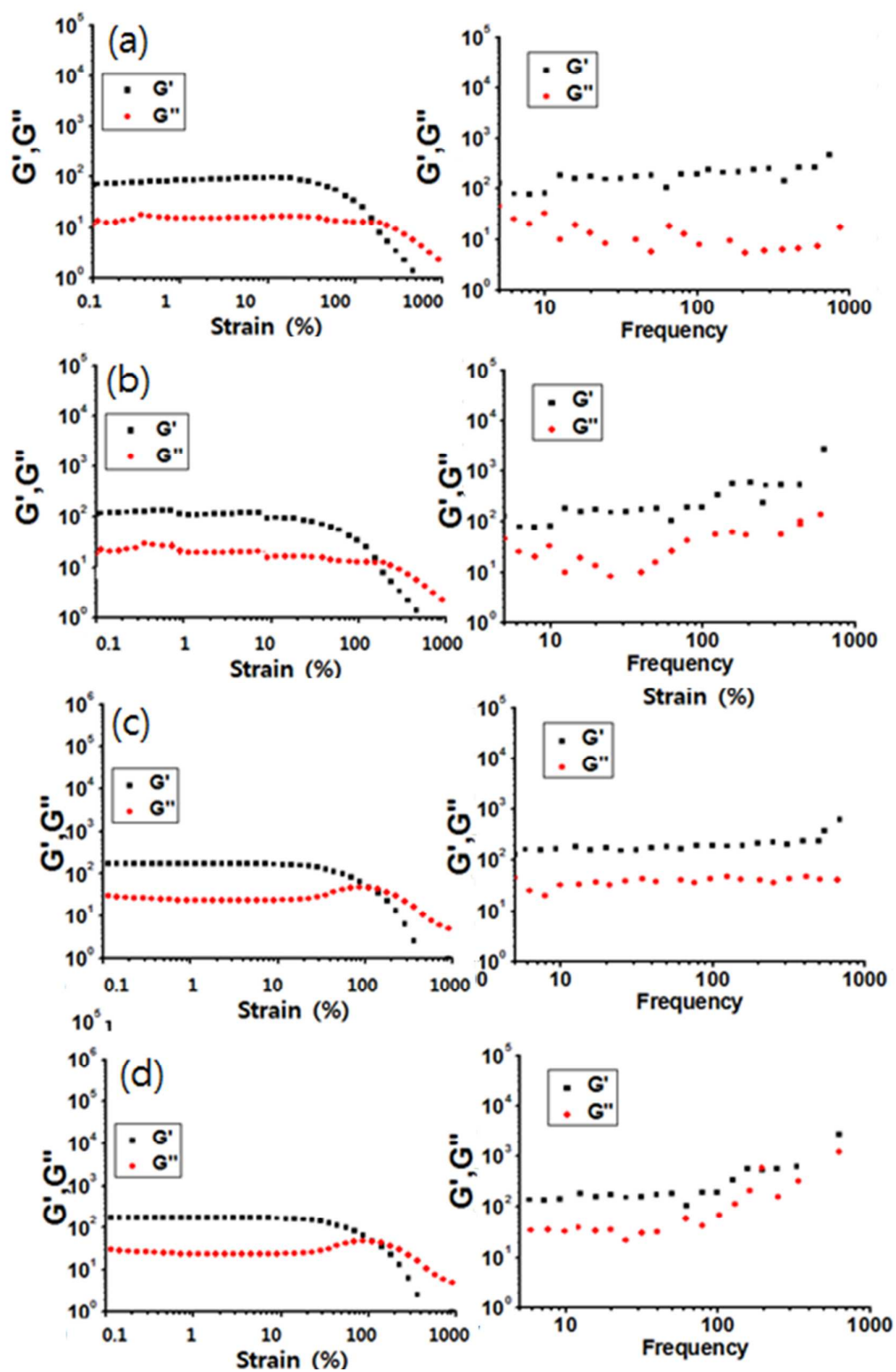


Figure S12. Rheological properties of gel obtained in acidic condition after aging for (a) 48 hr, (b) 72 hr, (c) 96 hr and (d) 128 hr (left: strain sweep tests at 0.1-1000%, right: frequency sweep tests at 5-1000 Hz).

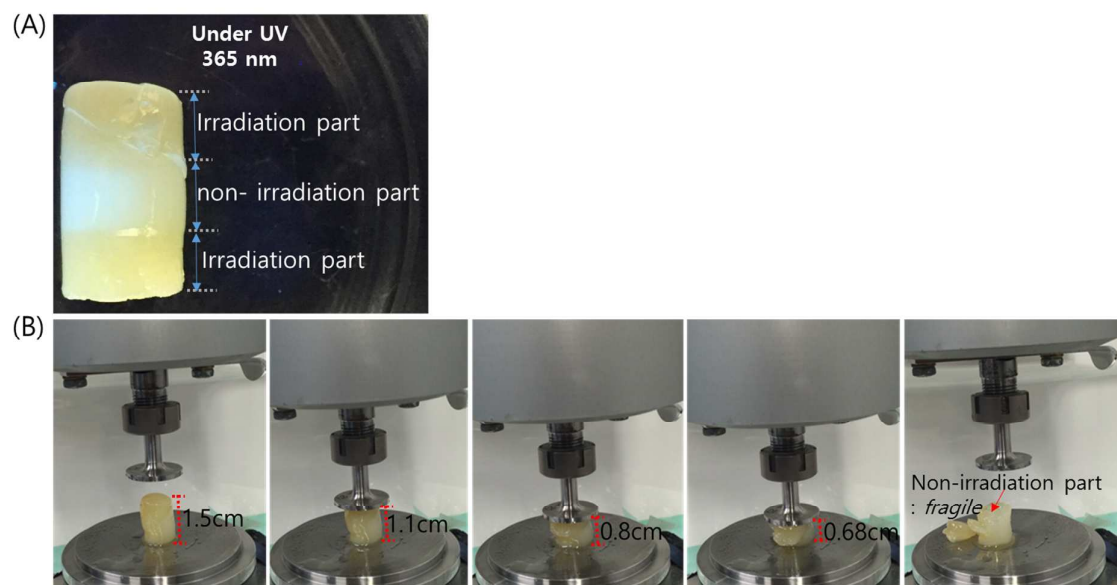


Figure S13. (A) Photograph of cylindrical gel sample with spatially controlled UV irradiation of the top and bottom. (B) Photographs of shape changes and resulting cleavage of the gel at the site that had not undergone UV irradiation (images corresponding to Movie S2).

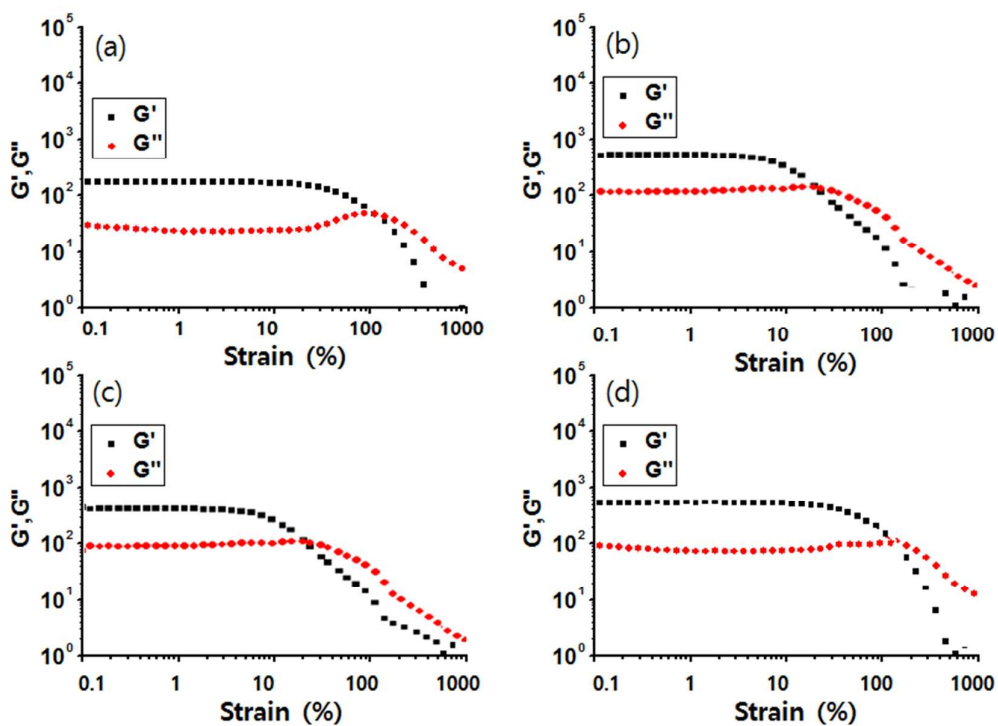


Figure S14. Results of strain sweep experiments for gel obtained in acidic condition at (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C for 1hr.

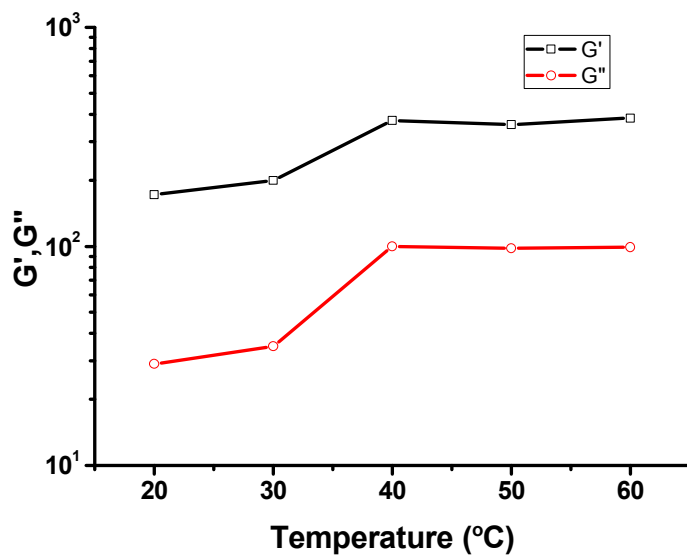


Figure S15. Plot of the elastic and storage moduli for a gel in acidic conditions after aging for 1 hour at different temperature aging (20 °C, 30 °C, 40 °C, 50 °C and 60 °C).

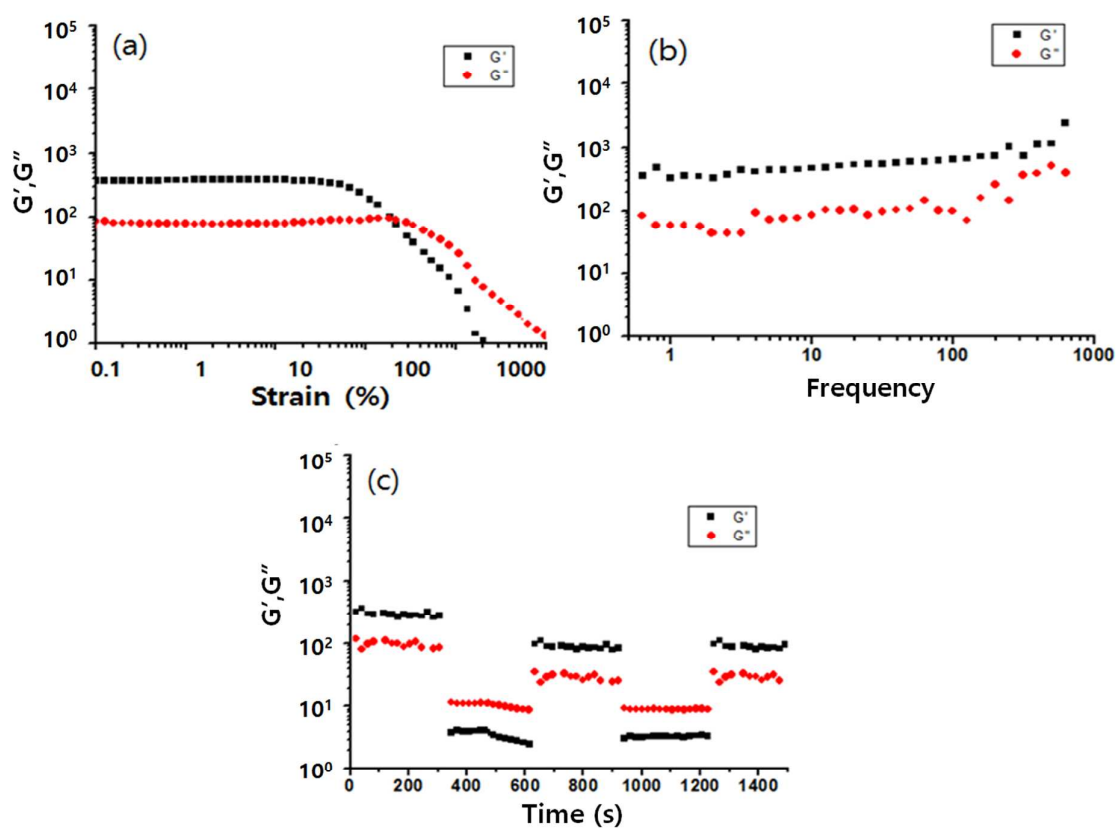


Figure S16. Rheological properties of gel obtained in acidic condition after heating for 1 hr at 60°C; (a) strain sweep tests at 0.1-10000 %, (b) frequency sweep tests at 0.5-1000 Hz, and (c) continuous step strain test at 0.1 % and 1000 %.

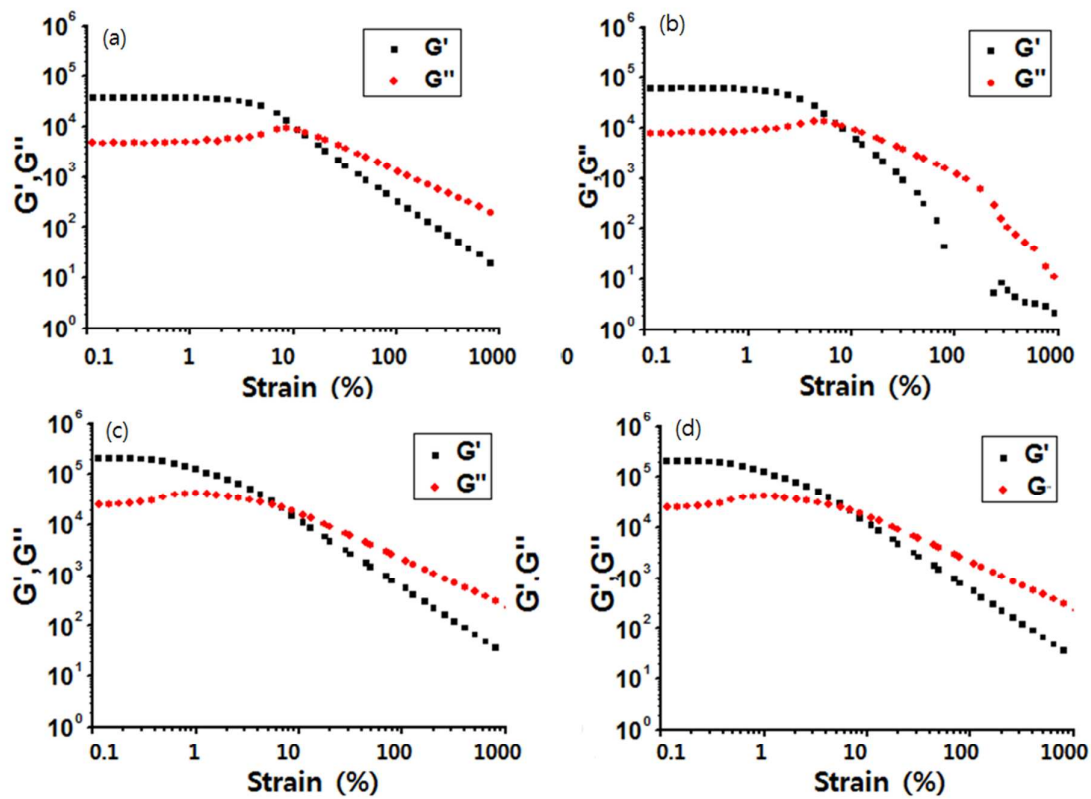


Figure S17. Strain sweep test results of gel obtained in acidic condition under UV irradiation for (a) 24 hr, (b) 48 hr, (c) 72 hr and (d) 96 hr (strain sweep tests at 0.1-1000).

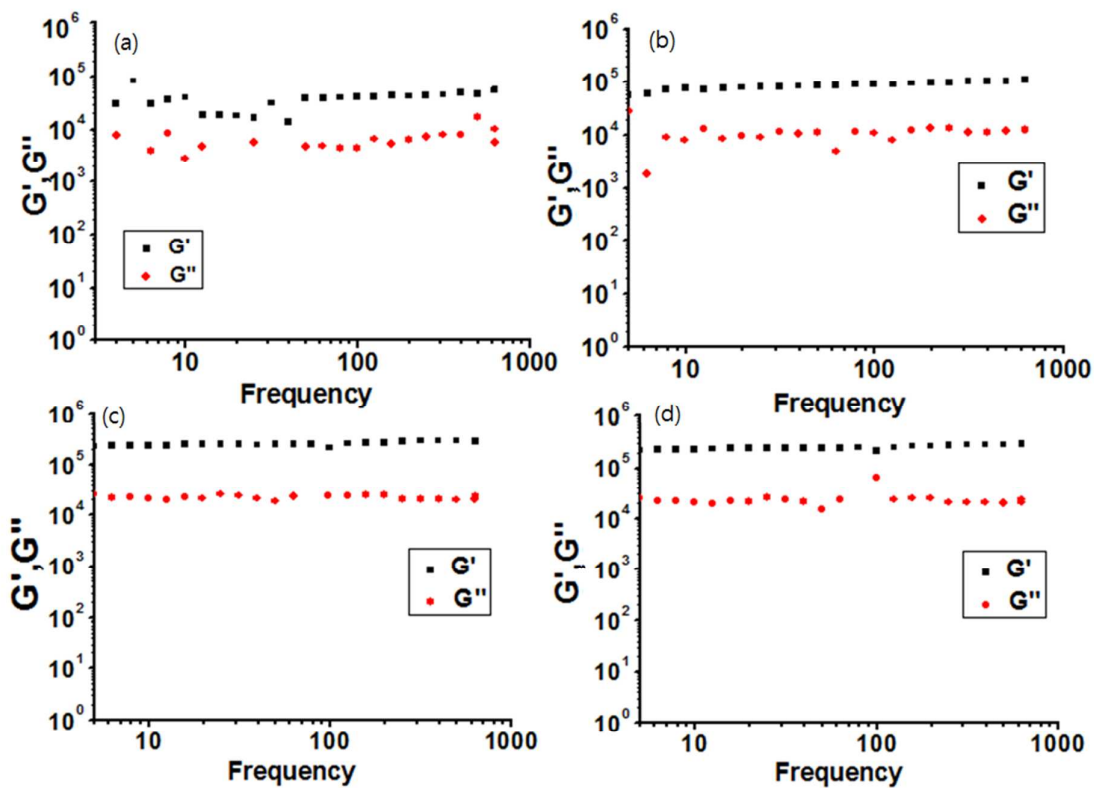


Figure S18. Frequency sweep test results of gel obtained in acidic condition under UV irradiation for (a) 24 hr, (b) 48 hr, (c) 72 hr and (d) 96 hr (frequency sweep tests at 5-1000 Hz).

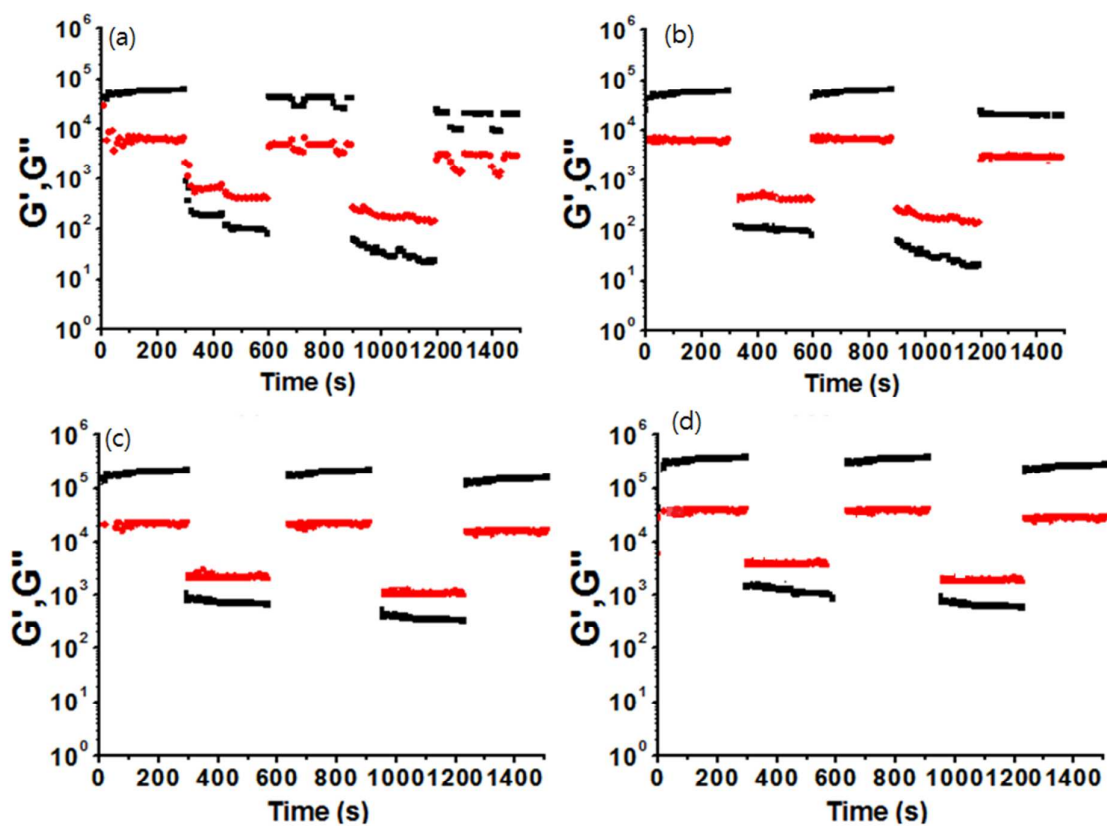


Figure S19. Continuous step strain test results of gel obtained in acidic condition under UV irradiation for (a) 24 hr, (b) 48 hr, (c) 72 hr and (d) 96 hr (continuous step strain test at 0.1 % and 100 %).

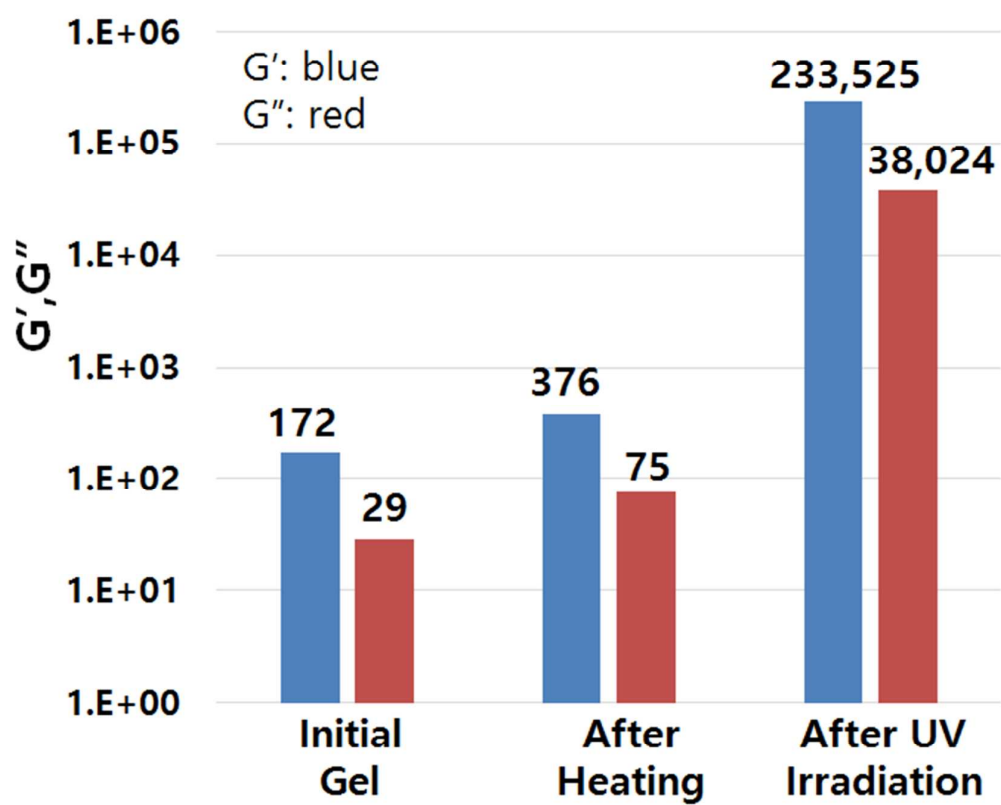


Figure S20. Plot of rheological properties of gel formed in acidic conditions before and after heating for 1hr at 60°C and UV irradiation for 96 hr.

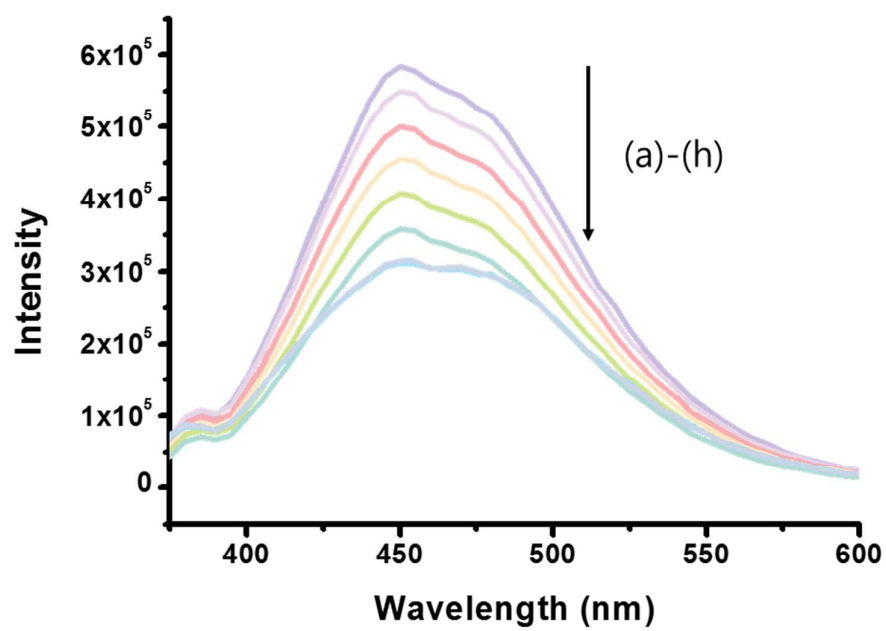


Figure S21. Fluorescence spectra of gel with photomask under UV irradiation for (a) 4hr, (b) 7hr, (c) 8hr, (d) 9hr (e) 10hr, (f) 11hr (g) 12hr and (h) 14hr.

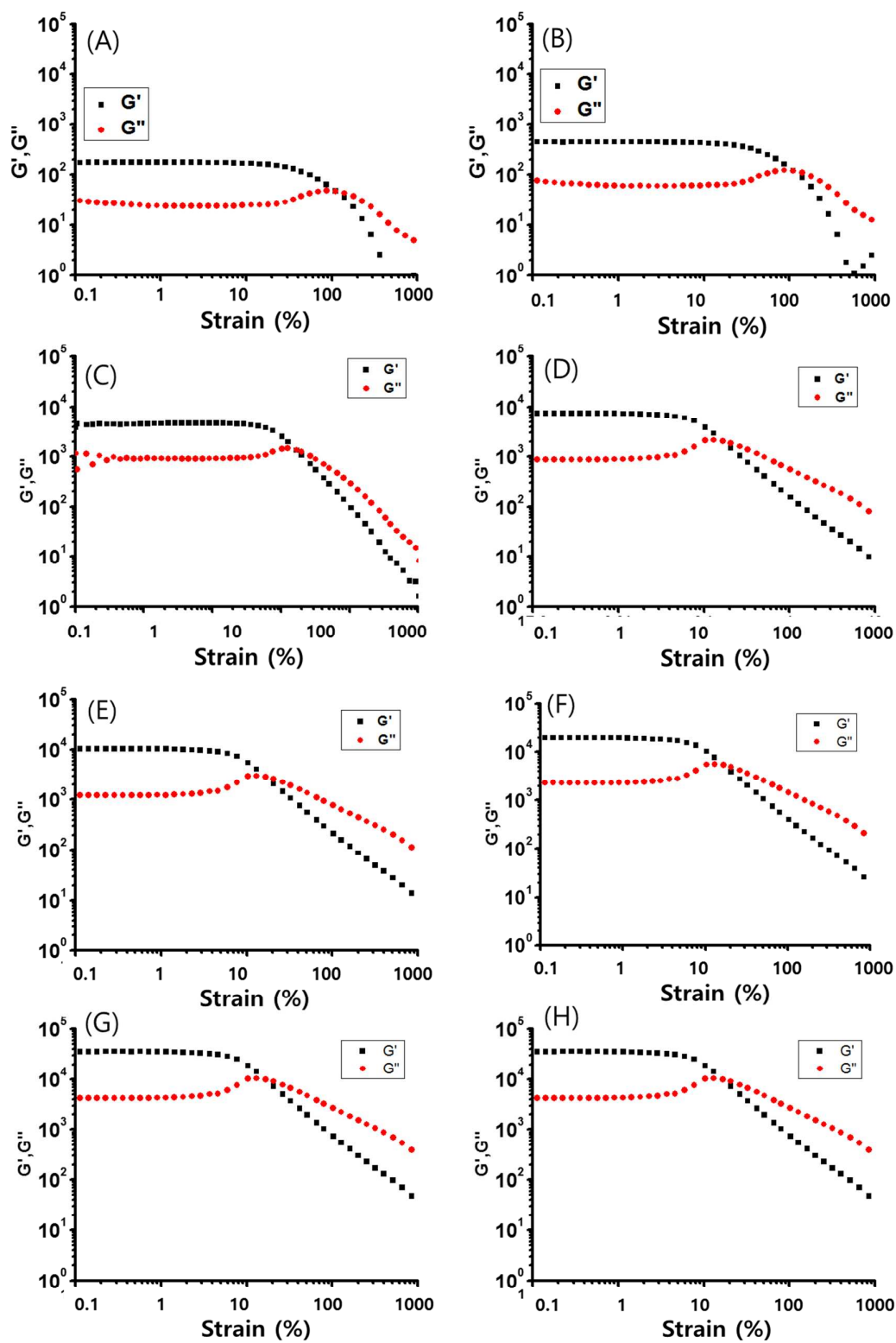


Figure S22. Strain sweep test results of gel with photomask under UV irradiation for (a) 4hr, (b) 7hr, (c) 8hr, (d) 9hr (e) 10hr, (f) 11hr (g) 12hr and (h) 14hr.

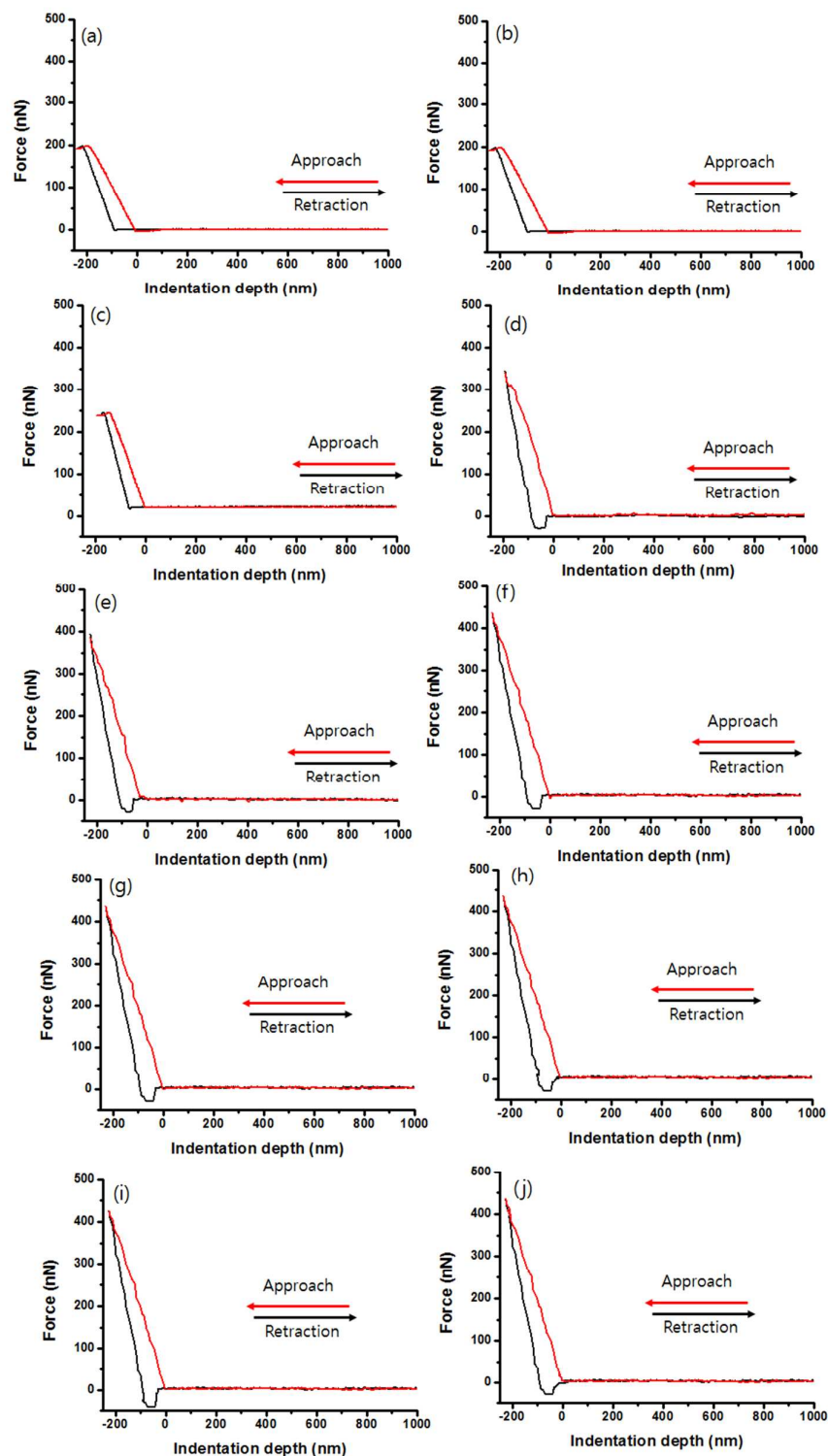


Figure S23. Approach and retraction force-displacement curves of gel after UV irradiation for (A) 6hr, (B) 9hr, (C) 12hr, (D) 15hr, (E) 18hr, (F) 24hr, (g) 28hr, (h) 34hr (i) 39hr (j) 48hr (the curves for gels prepared with less than 5 hr of UV irradiation time did not provide reproducible data due to a problem associated with weak visco-elasticity during the tip approach to the gel surface).

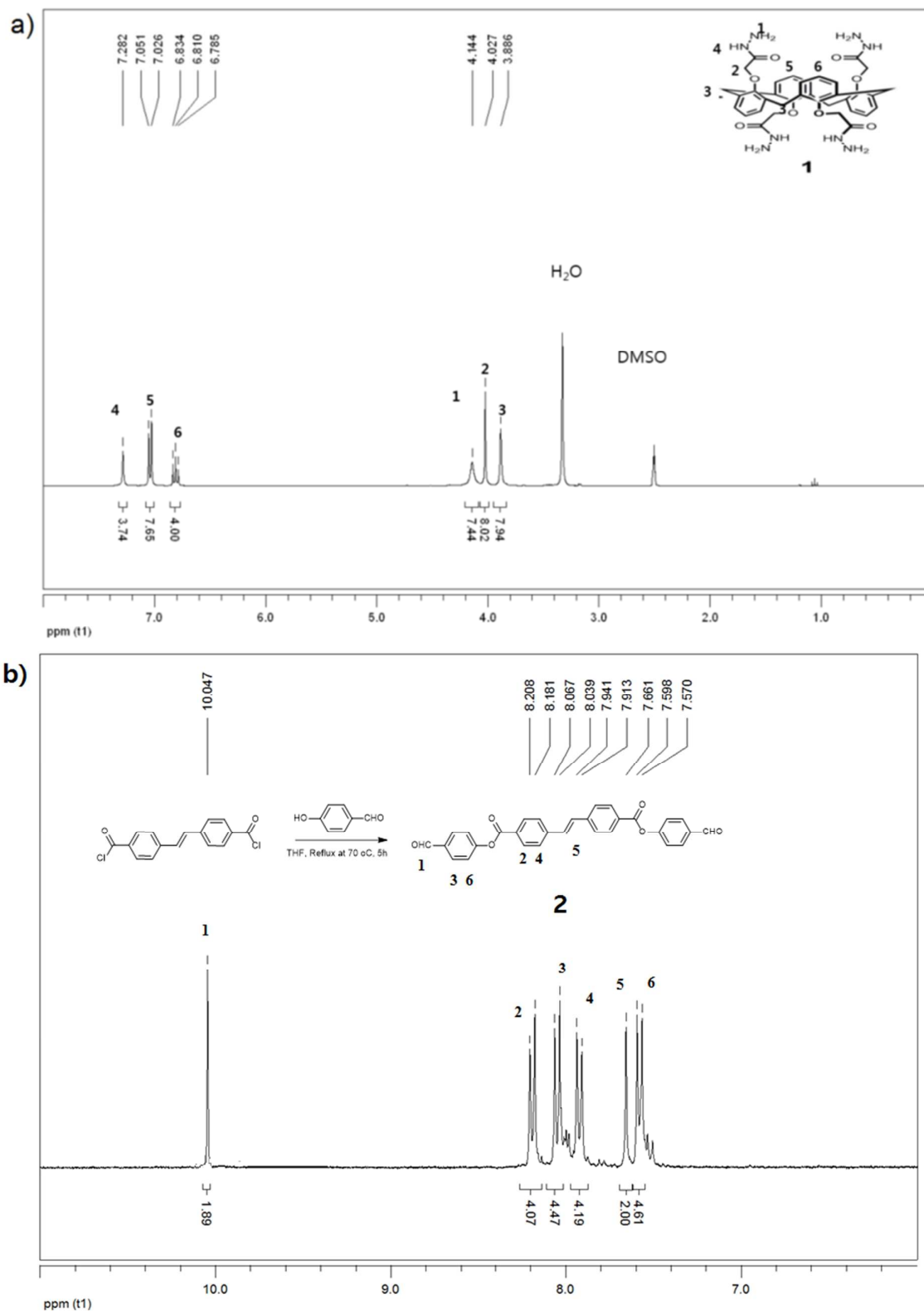


Figure S24. NMR spectra of compound **1** and compound **2**.