

Supplementary information

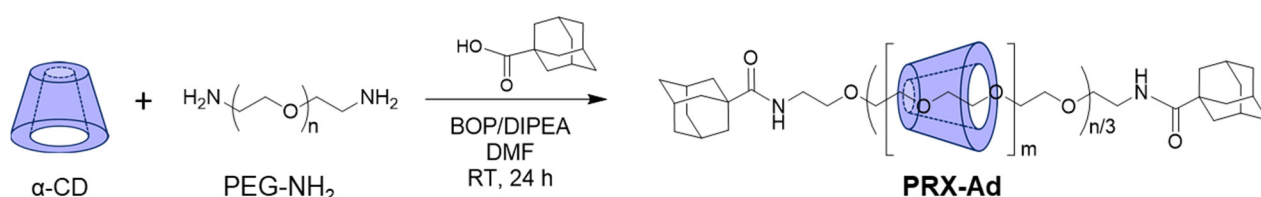
**Visible light-degradable supramolecular gels comprising cross-linked  
polyrotaxanes capped by trithiocarbonate groups**

Tae Woong Kang, Atsushi Tamura\*, Yoshinori Arisaka, Nobuhiko Yui

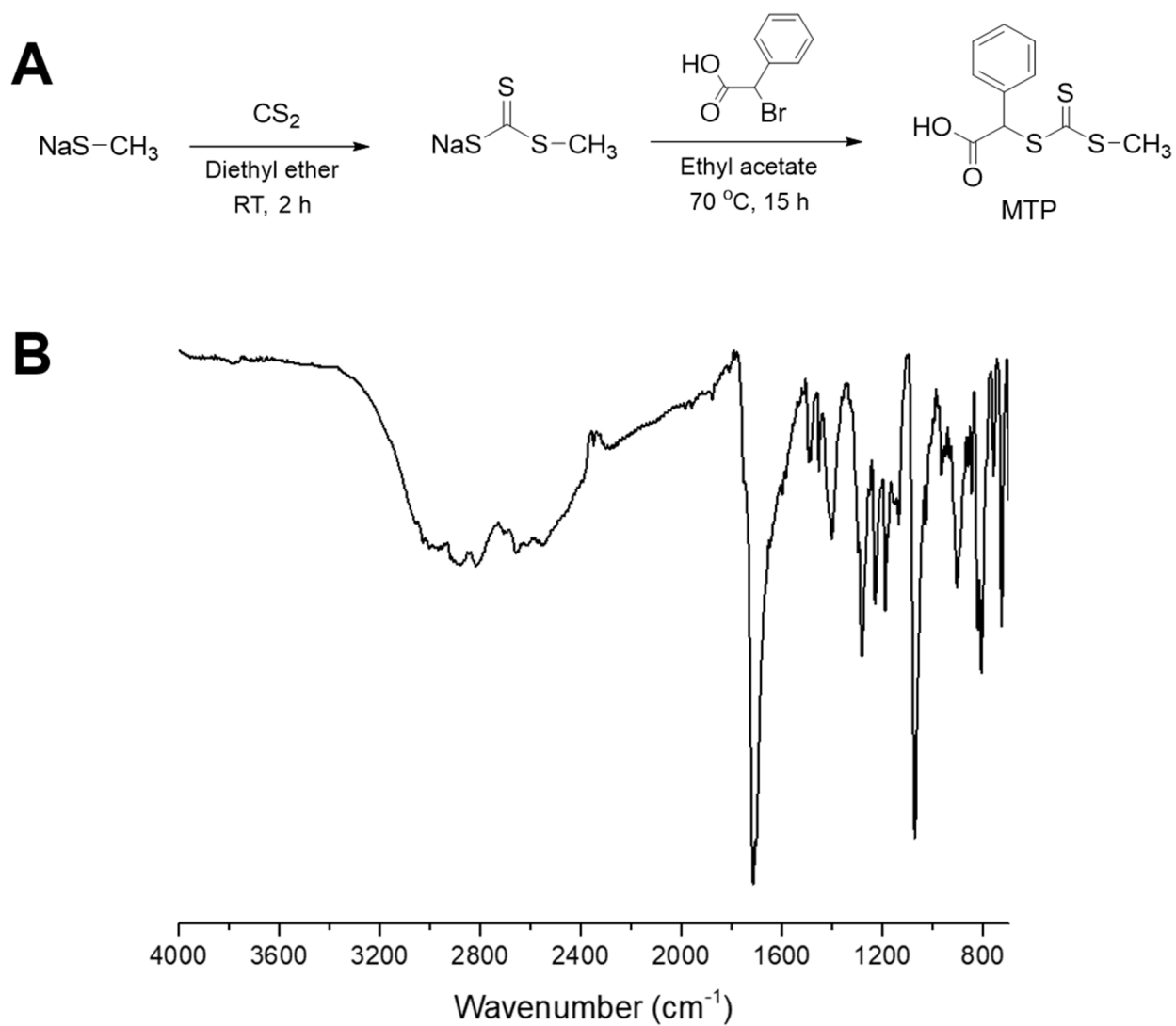
Department of Organic Biomaterials, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University (TMDU), 2-3-10 Kanda-Surugadai, Chiyoda, Tokyo 101-0062, Japan.

\*Corresponding author: Dr. Atsushi Tamura (E-mail: tamura.org@tmd.ac.jp)

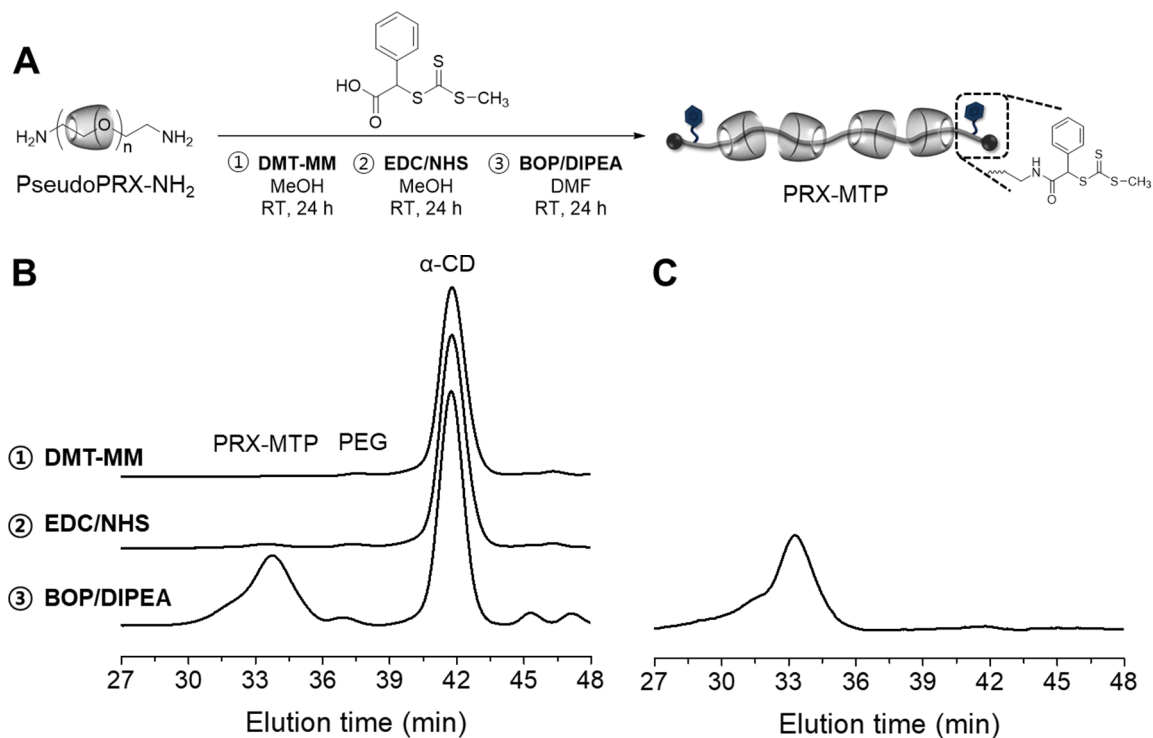
**Synthesis of 1-admantyl group-capped polyrotaxane (10kPRX-Ad)**



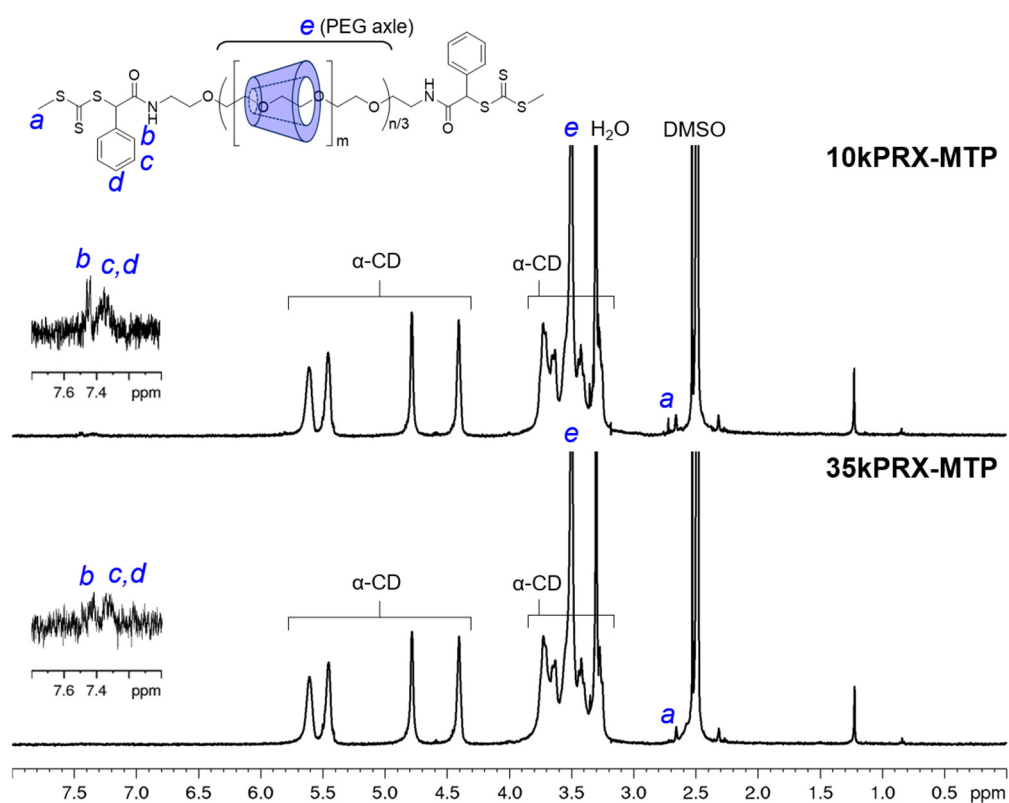
10kPEG-NH<sub>2</sub> (4.0 g, 0.4 mmol) and  $\alpha$ -CD (12.1 g, 12.4 mmol) were dissolved in distilled water (82.7 mL) and the solution was stirred for 24 h at room temperature. The precipitate was collected by centrifugation and freeze-dried to obtain a pseudo-PRX as a white solid (12.84 g). 1-Adamantanecarboxylic acid (0.72 g, 3.98 mmol), BOP (1.77 g, 4.05 mmol), and DIPEA (0.68 mL, 4.01 mmol) were then dissolved in DMF (120 mL), and the solution was added into a glass bottle with pseudo-PRX. The mixture was stirred for 24 h at room temperature. After the reaction, the precipitate was collected by centrifugation, and the precipitate was washed 3 times with DMF. The washed precipitate then dissolved in a small aliquot of DMSO, and reprecipitated 3 times in distilled water. The recovered precipitate was freeze-dried for 2 days to obtain 10kPRX-Ad (6.76 g, 29.9 % yield based on PEG).



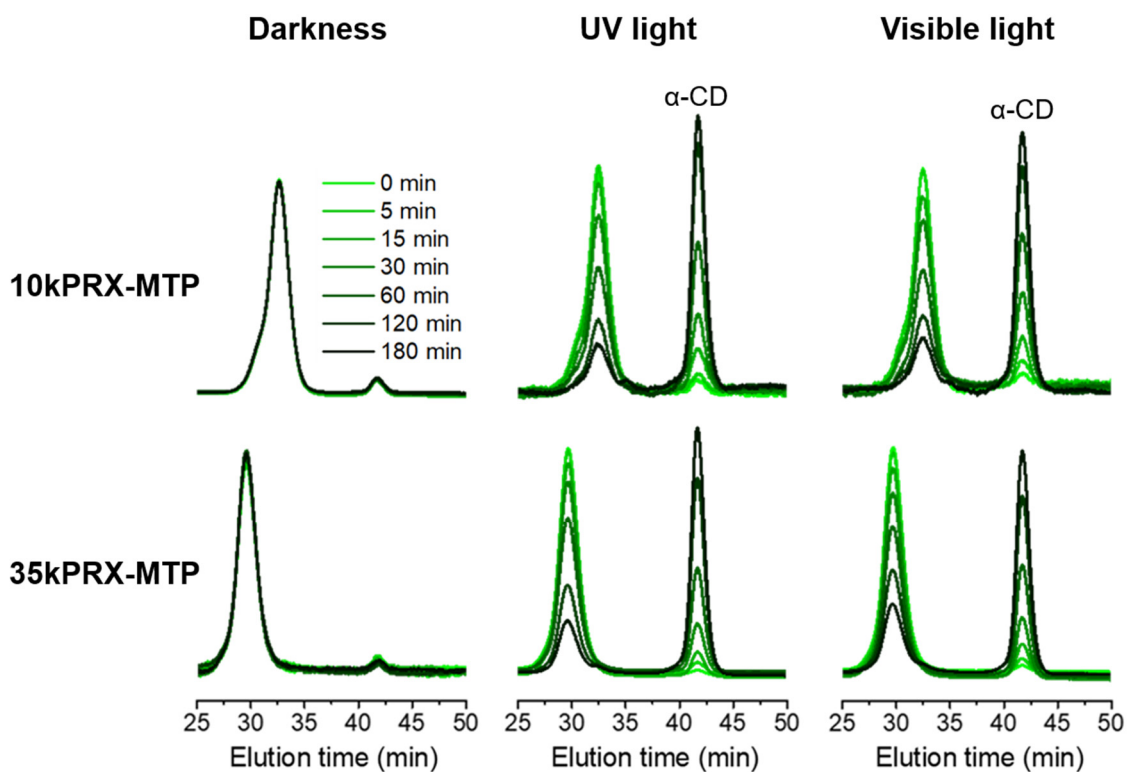
**Figure S1.** (A) Synthesis scheme of MTP. (B) FT-IR spectrum of MTP.



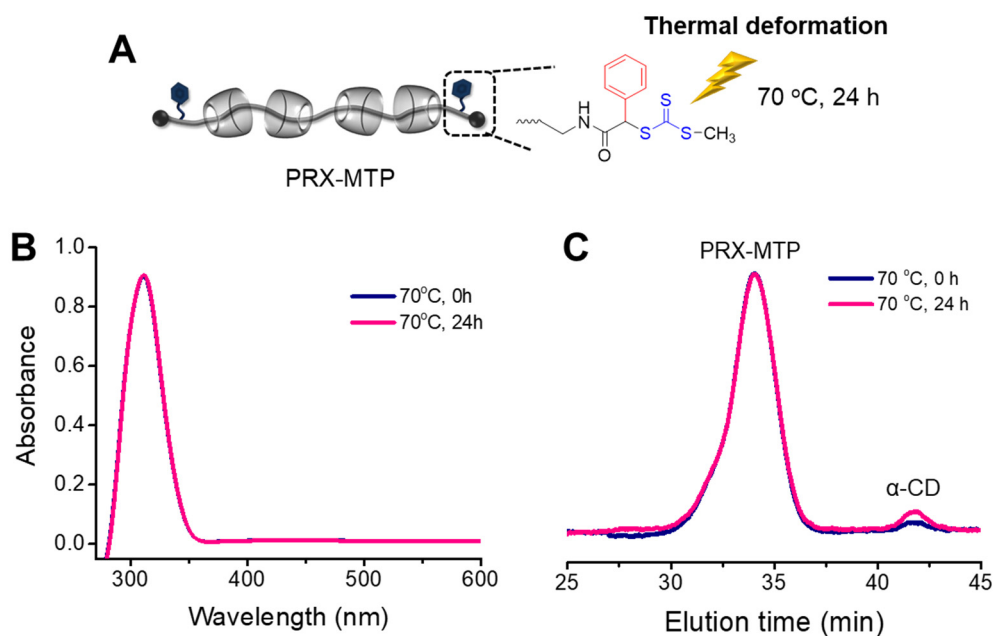
**Figure S2.** (A) Synthesis methods of PRX-MTP using different types of condensation reagents (DMT-MM, EDC/NHS, or BOP/DIPEA). (B, C) SEC curve of crude material before (B) and after washing (C).



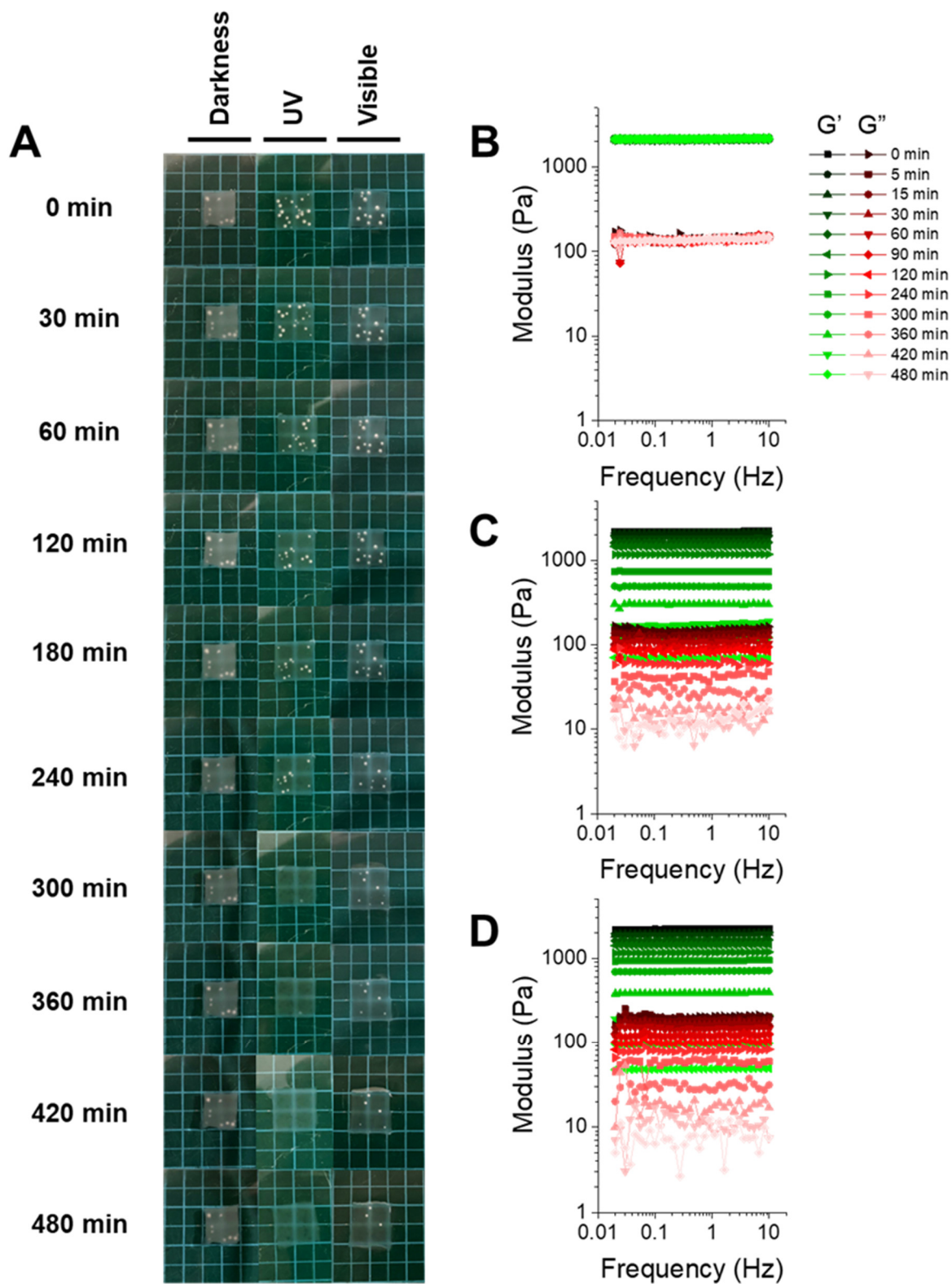
**Figure S3.**  $^1\text{H}$  NMR spectra of 10kPRX-MTP and 35kPRX-MTP in  $\text{DMSO-}d_6$ .



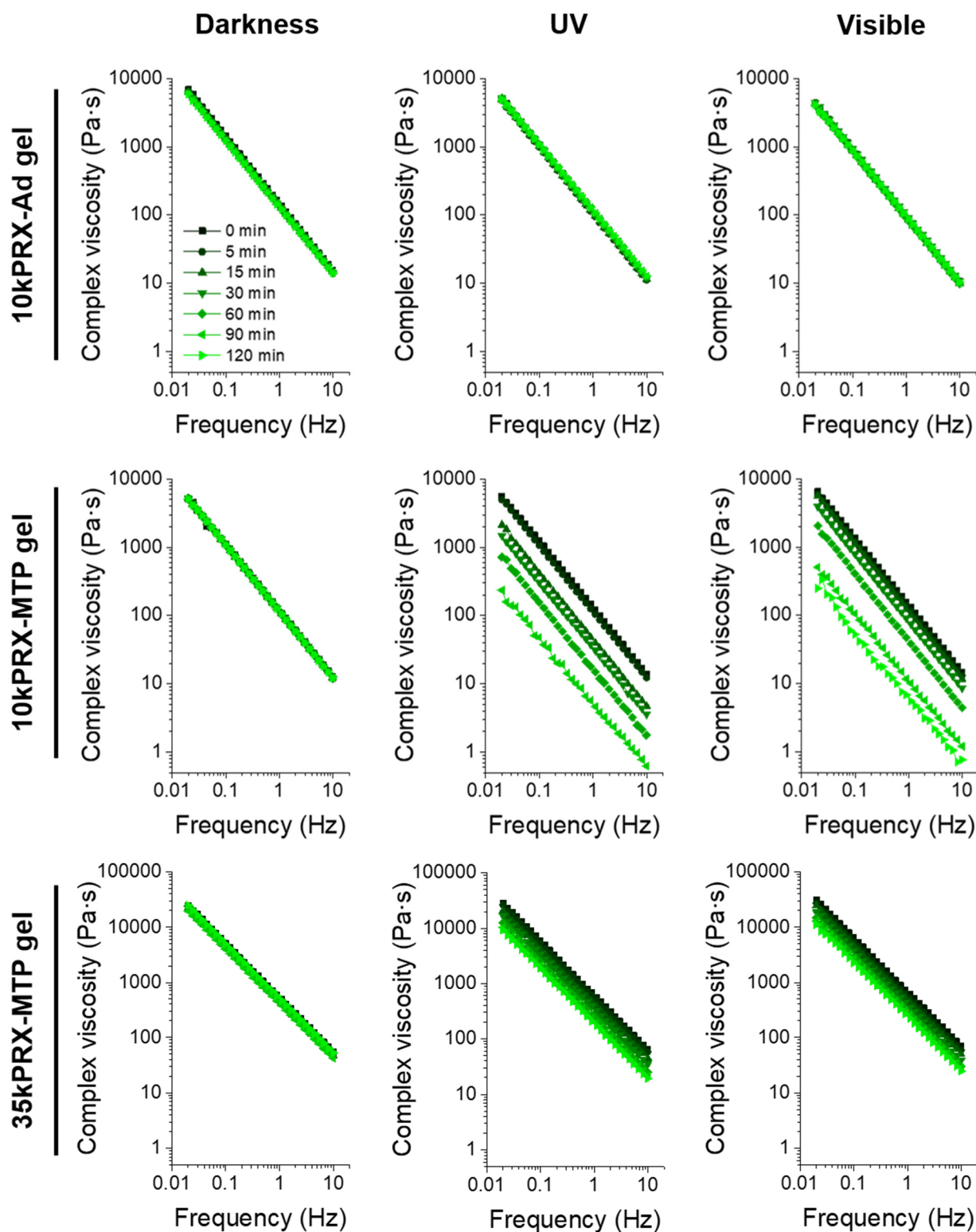
**Figure S4.** SEC curves (RI detection) of 10kPRX-MTP and 35kPRX-MTP under dark conditions or irradiation with UV and visible light for 180 min.



**Figure S5.** (A) UV-vis absorption spectra and (B) SEC curves of PRX-MTP before and after heating at 70 °C for 24 h.



**Figure S6.** (A) Images of 35kPRX-MTP gels under dark condition or irradiation with UV and visible light for 0–480 min. (B–C) Storage ( $G'$ ) and loss moduli ( $G''$ ) of 35kPRX-MTP gels under dark conditions (B) or irradiation with UV (C) and visible light (D) for 480 min.



**Figure S7.** Complex viscosities of 10kPRX-Ad gels, 10kPRX-MTP gels, and 35kPRX-MTP gels under darkness, UV irradiation, and visible light irradiation for 120 min.