

Supplementary Information for:
“Bio-inspired metal-coordinate hydrogels with programmable
viscoelastic material functions controlled by longwave UV light”

Scott C. Grindy and Niels Holten-Andersen

Department of Materials Science and Engineering, Massachusetts Institute of Technology,
Cambridge, MA, USA

Correspondence: holten@mit.edu

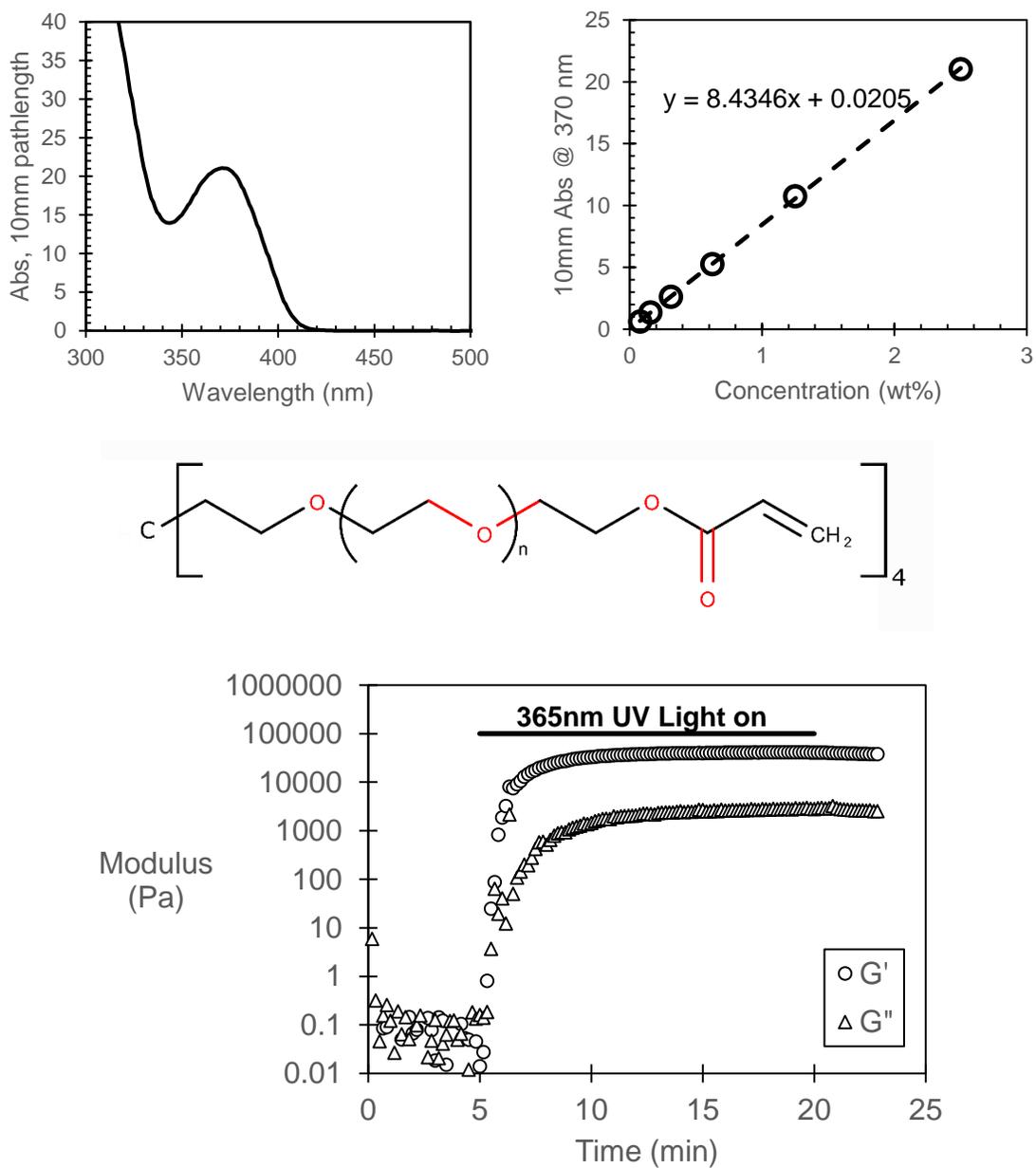


Figure S1: Characterization of LAP photoinitiator. (a) UV-vis absorption of a 2.5wt% solution of LAP shows the strong absorbance band at ca. 350-400nm, and (b) its characteristic absorbance is linearly proportional to its concentration. (c) We confirmed the functionality of LAP by using it to photopolymerize a 10wt%, 10kDa 4-arm PEG-acrylate hydrogel (structure above figure). The gel point occurs within ~2-3 minutes after initiating UV-irradiation, and full cure of the gel on our apparatus occurs in approximately 5-10 minutes as measured by G' (1 rad/s).

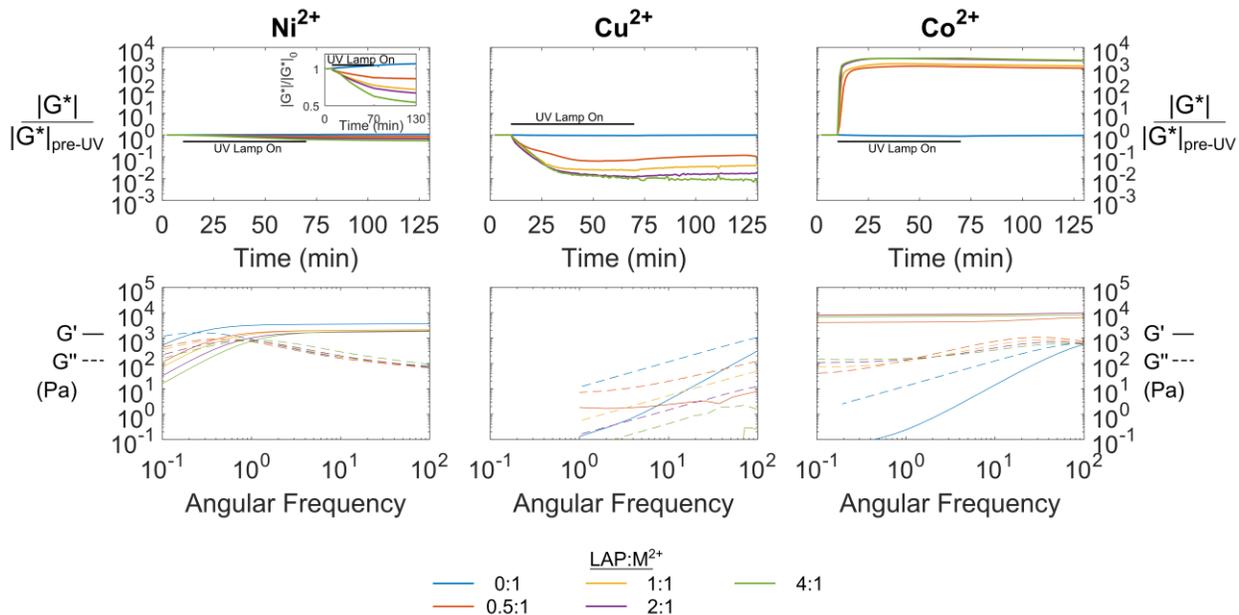


Figure S2: Mechanical properties of hydrogels with increased LAP loading. While using additional LAP further decreases the moduli and relaxation time of 4PEG-His:Ni hydrogels, the effect pales in comparison to the effects observed in Cu-crosslinked or Co-crosslinked hydrogels.

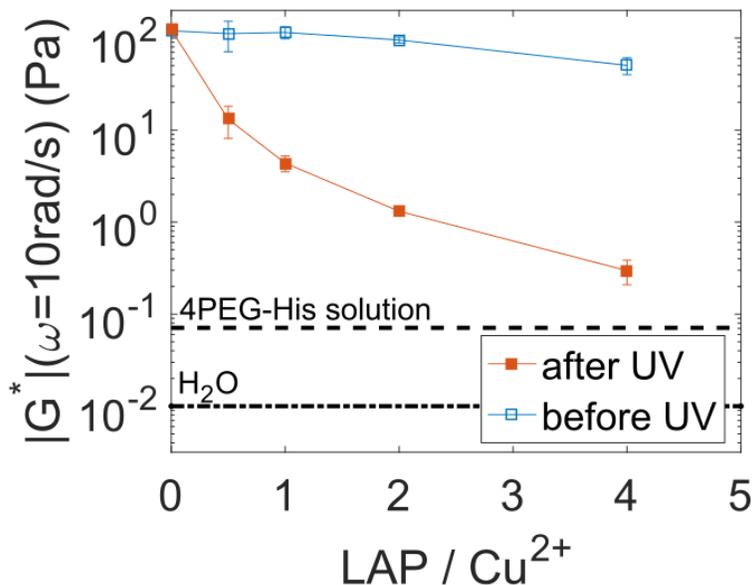


Figure S3: LAP-concentration dependence of $|G^*| = \sqrt{G'^2 + G''^2}$ at $\omega = 10 \text{ rad/s}$ for 4PEG-His:Cu hydrogels. Even at the highest LAP loading measured here, the modulus of 4PEG-His:Cu hydrogels is still higher than the 4PEG-His solution itself, suggesting that His:Cu crosslinks still exist after UV-irradiation. An estimate of the modulus of H₂O is provided for reference (assuming $\eta_{H_2O} \approx 1 \text{ mPa} \cdot \text{s}$).

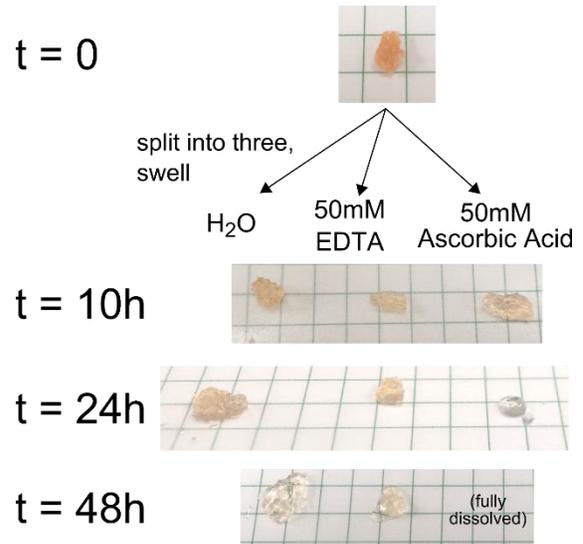
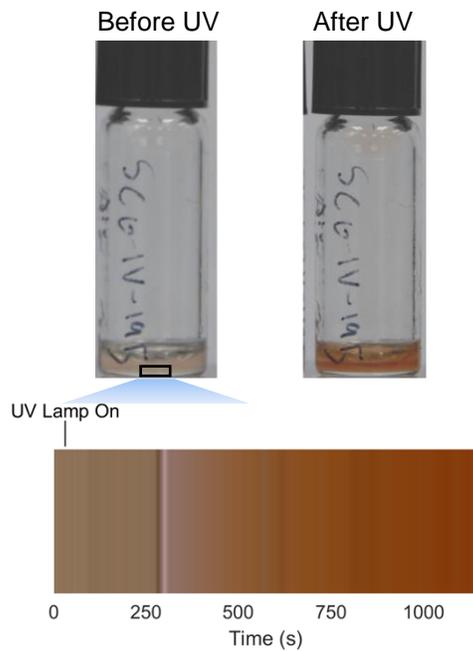


Figure S4: Evidence for Co^{3+} oxidation.

(left) UV-irradiation distinctly changes the color of 4PEG-His:Co:LAP hydrogels. The lower figure zooms in on how the color changes over the course of UV irradiation.

(right) Ascorbic acid reduces Co^{3+} , dissolving hydrogels significantly faster than EDTA.

After 24 h, the hydrogel treated with ascorbic acid (a reducing agent) has lost its orange color, and after 48 h it is fully dissolved. In contrast, hydrogels treated with H_2O or ethylenediaminetetraacetic acid (EDTA, a strong, broad-spectrum metal chelator) do not dissolve after 48 h.

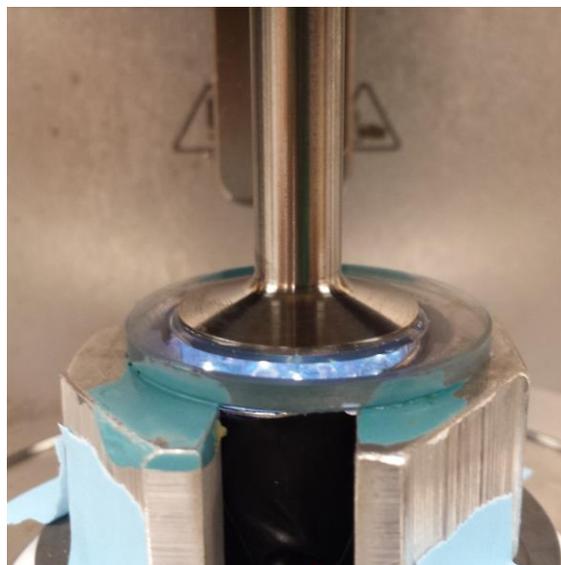
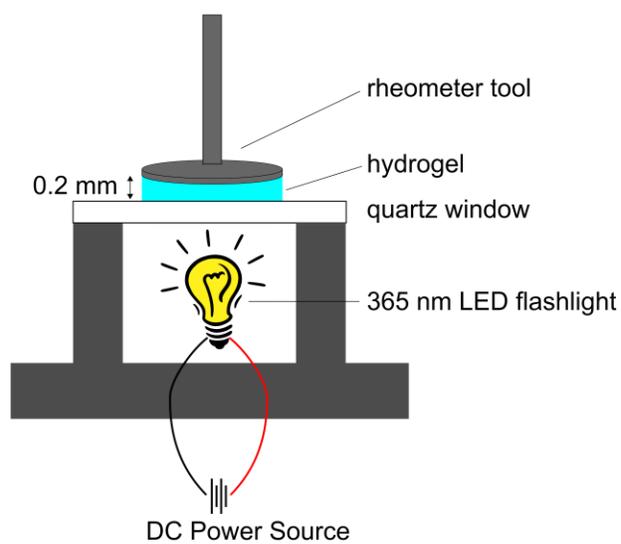


Figure S5: UV-rheology apparatus. The light source used is the “HQRP Longwave 12 LED UV Flashlight 365 nm” modified to be powered by a DC power source and to fit onto our rheometer.