

Supporting Information

3D UV printing with polymeric ionic liquid and its gold nanoparticle embedded composites.

Susana Ferrufino Amador,^a Rudy White,^a Olivia Downey,^a Kayla Foy,^a Rachel Wynn,^a Hawa Khan,^a Megan O'Neil,^b Olivia McNair,^b and Samrat Dutta^{*a}

^b *School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, MS 39406 USA*

^a *Department of Chemistry, Xavier University of Louisiana, New Orleans, LA 78125, USA.*

*Corresponding Author: sdutta@xula.edu

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S1. Characterization of Monomer

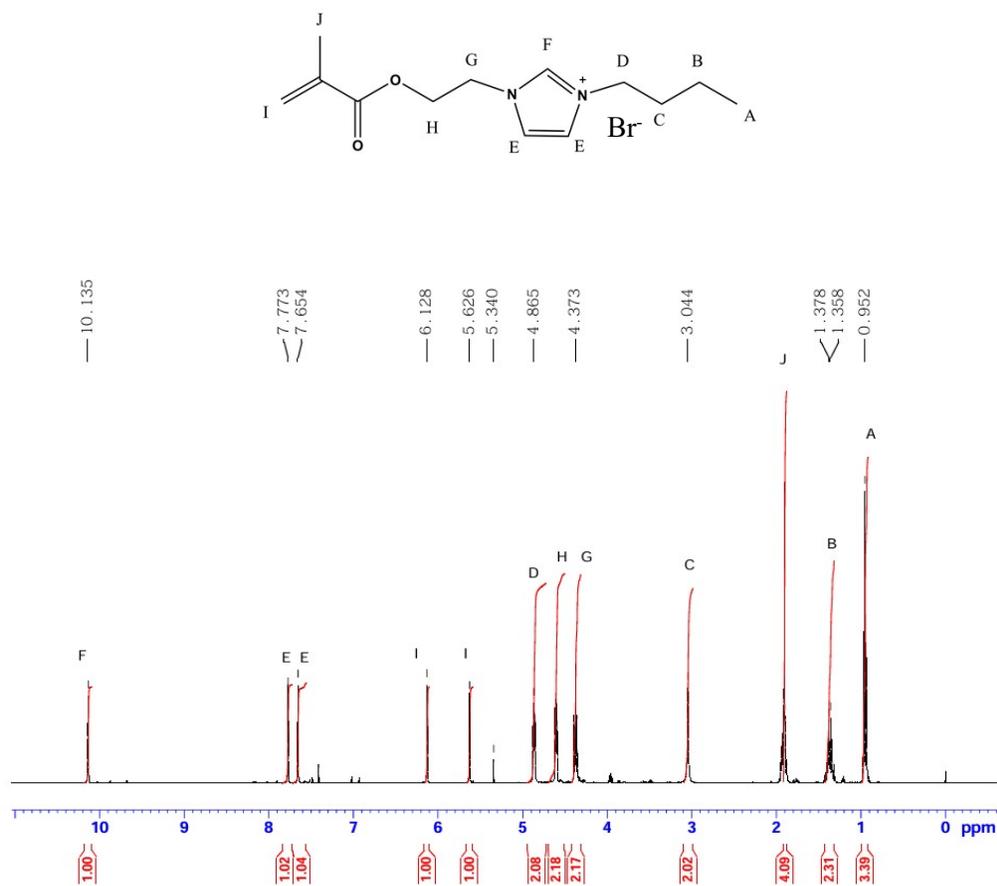


Figure S1. NMR (400 MHz, DMSO) of the monomer.

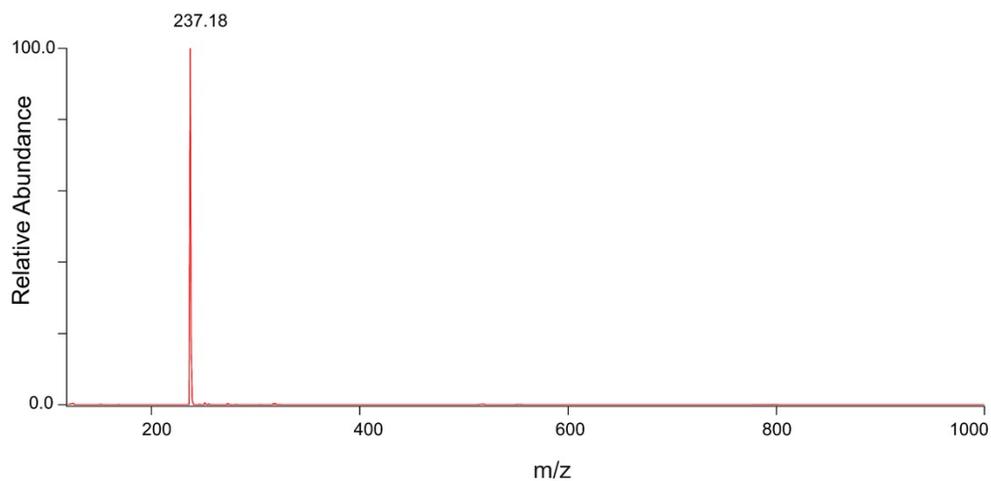


Figure S2. ESI-MS (positive ion mode) of the monomer(cation). The m/z (calculated) is 237.16 (cation) of the monomers, whereas the m/z (observed) is 237.18.

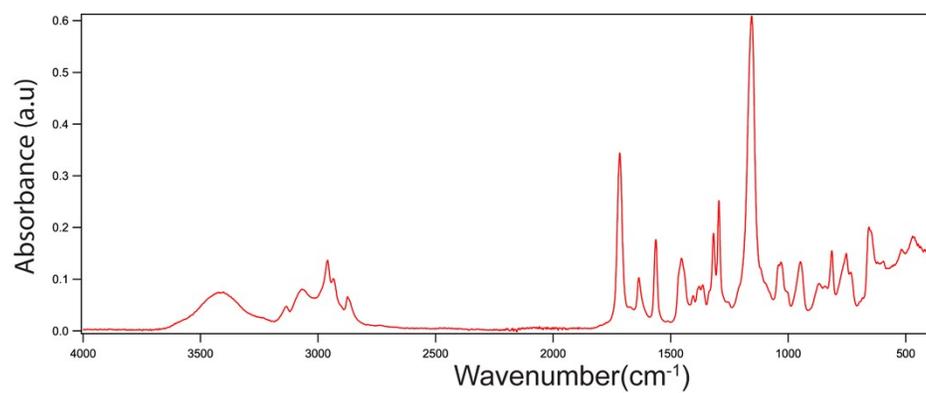


Figure S3. FTIR of the monomer in ATR mode.

S2. Characterization of Crosslinker

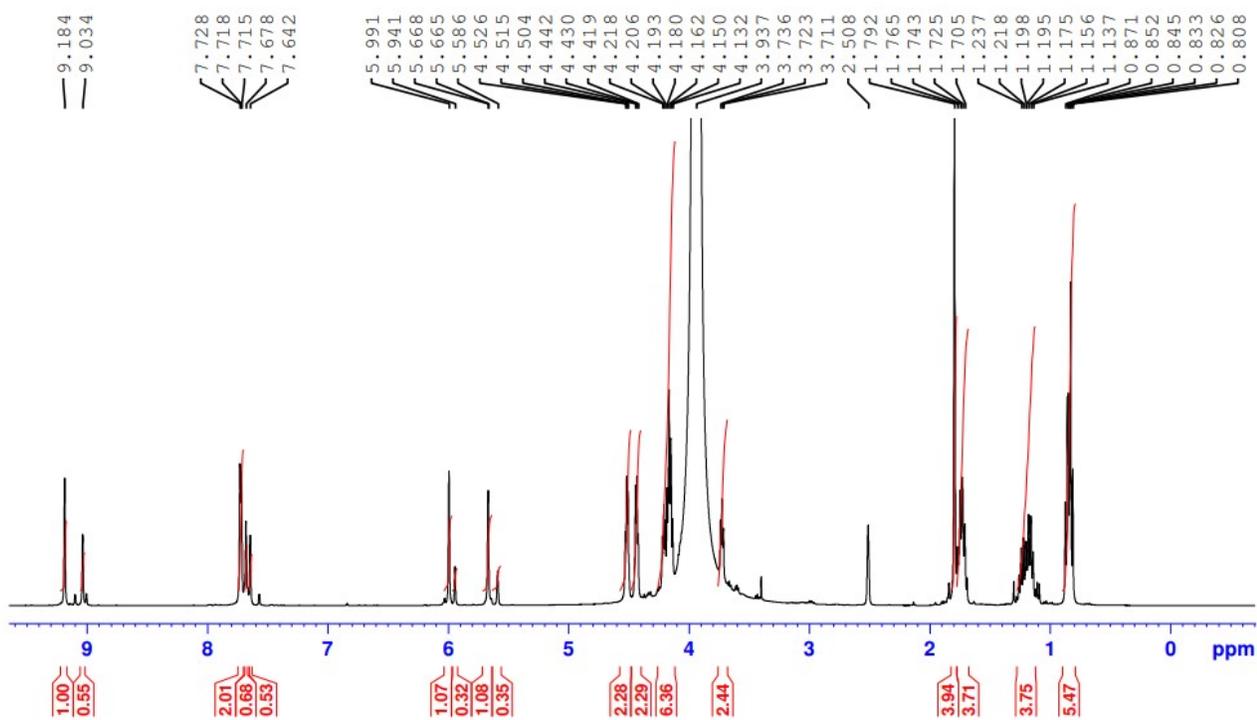
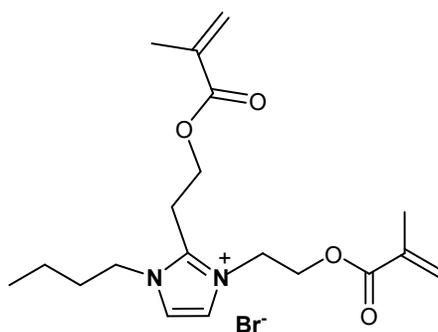


Figure S4. NMR (400 MHz, DMSO) of the crosslinker.

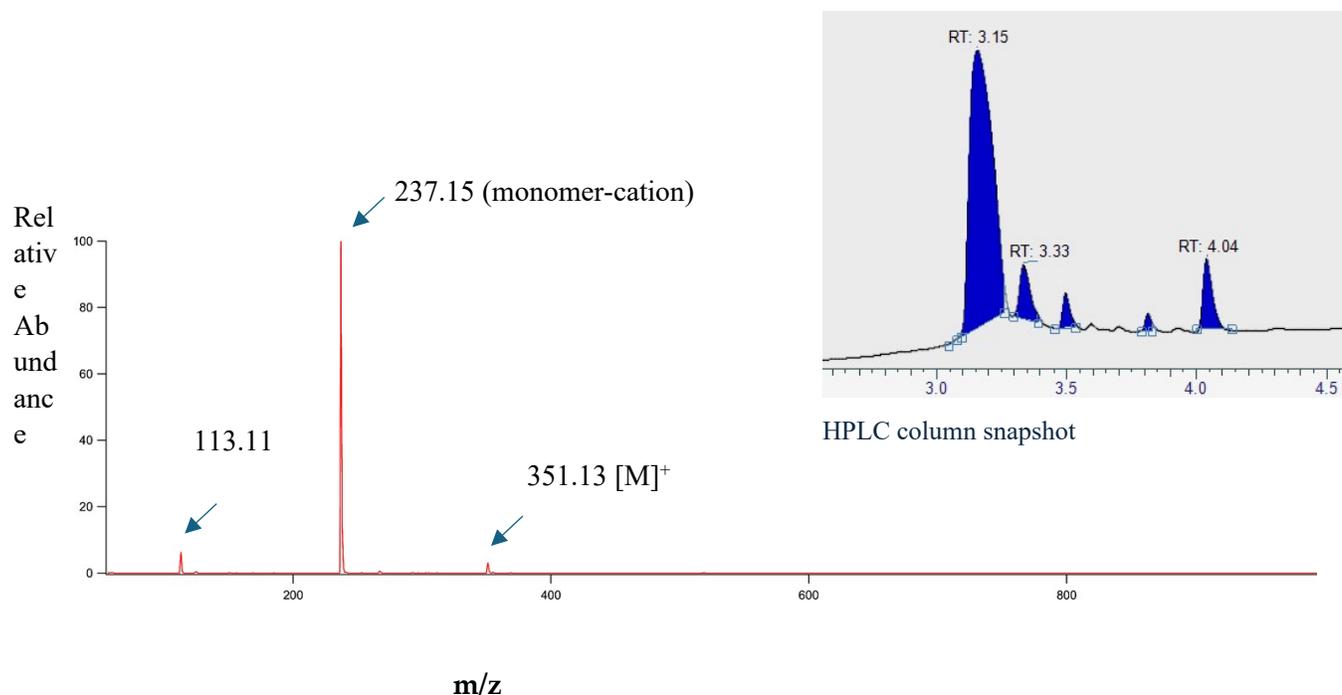


Figure S5. ESI-MS (positive ion mode) of the crosslinker(cation) from the HPLC column (shown in inset) with a retention time of 3.15 min, representing 85% of the relative peak volume. The m/z (calculated) is 349.53 (cation) of the monomers, whereas m/z (observed) is 351.13.

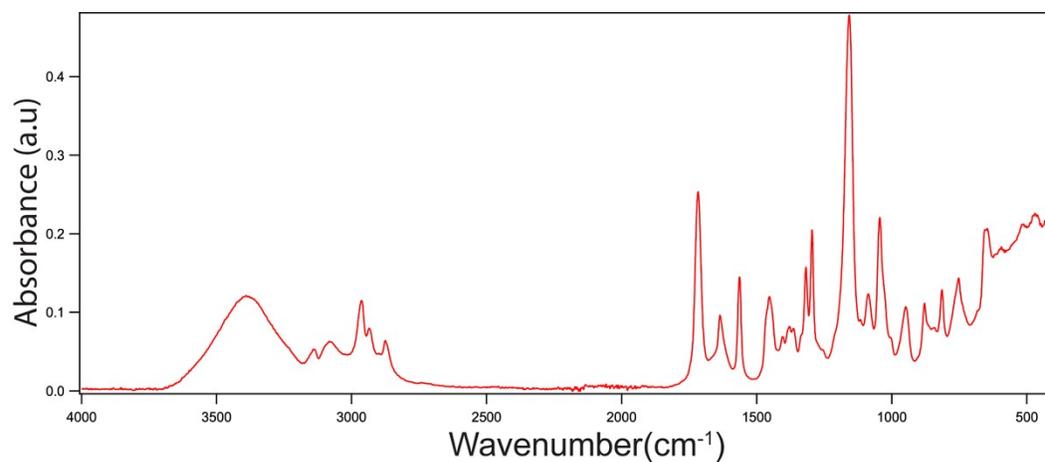
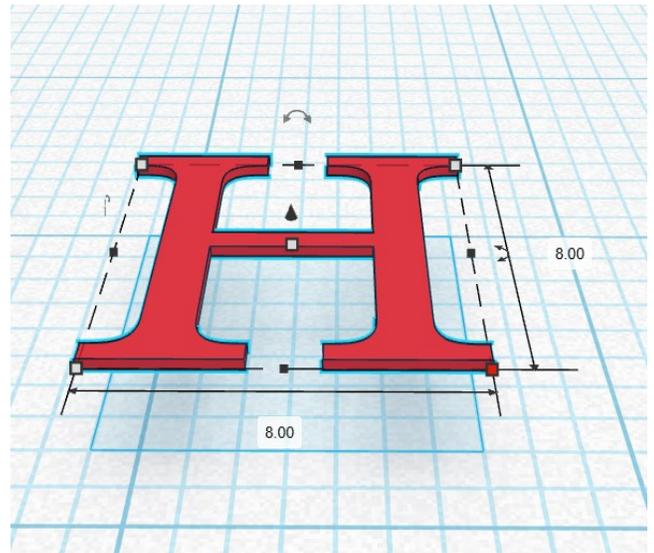
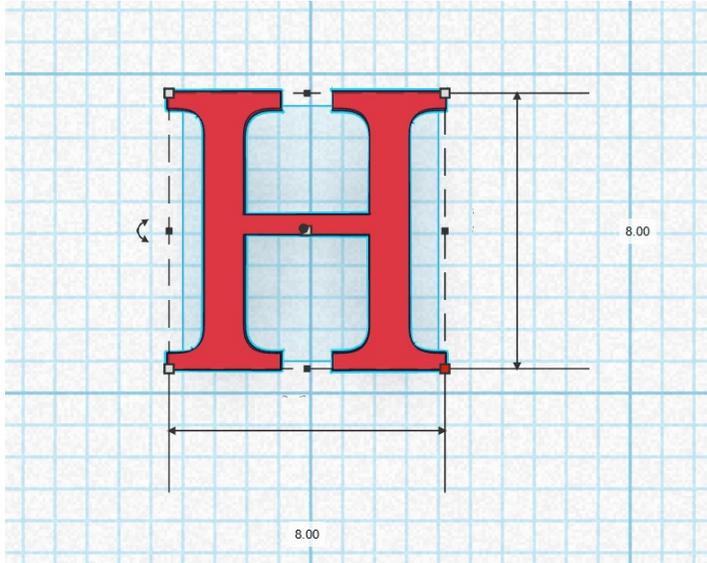


Figure S6. FTIR of the crosslinker in ATR mode.

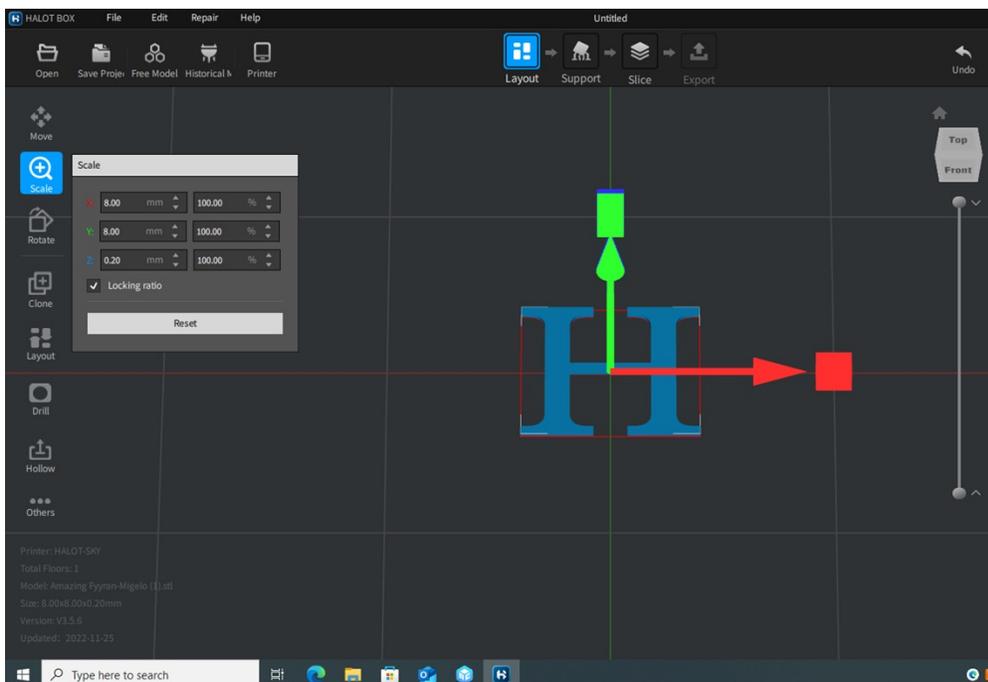
S3. Protocols for 3D printing.

Step 1. User-defined structures were built in TinkerCAD. Here is an example with the letter “H” using 80/20 ionic liquid



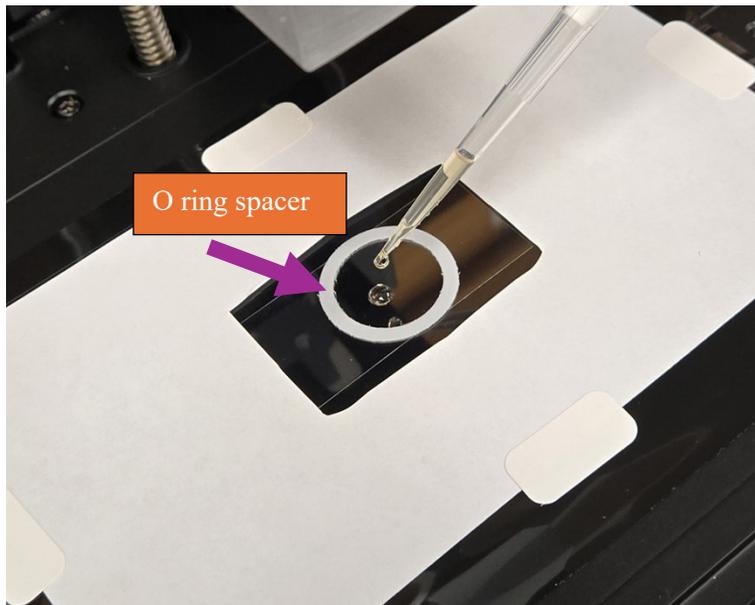
photocurable mixture.

In TinkerCAD, H is drawn. Note X and Y are 8 mm x 8mm. The file is then converted to .STL



Step 2. The above file is then sliced in HalotBox or Anycube slicer

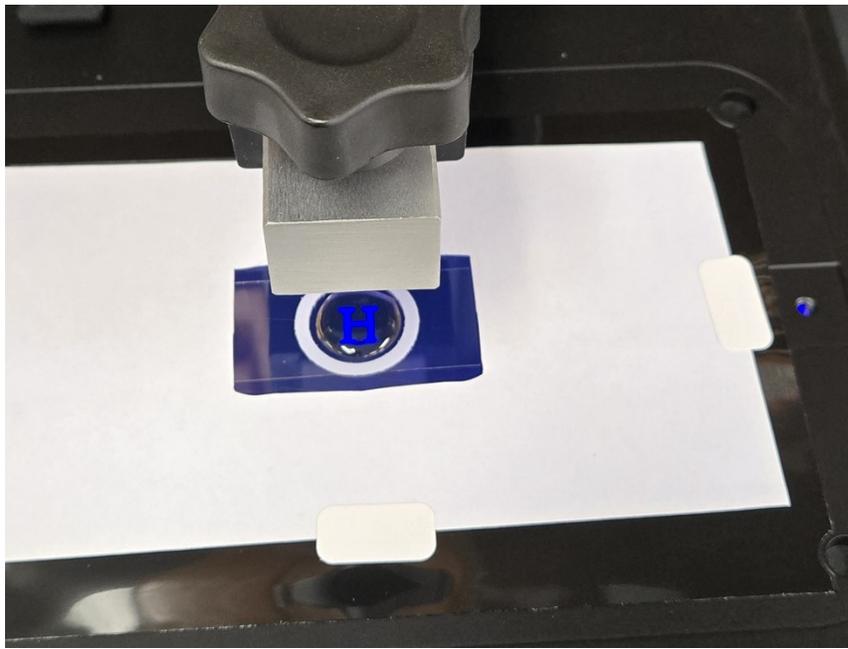
Step 3. The file is loaded on the printer. In parallel, we directly add the resin to the build glass plate. A paper cover is placed so that we can approximately know the center of the beam as



shown below.

The O-ring (200 to 500 μ m thickness) spacer acts as the vat. Note that we also use SecureSeal™ imaging spacers. Weights (not shown) are placed on the O-rings to prevent resin leakage.

Step 4. The file is then launched.

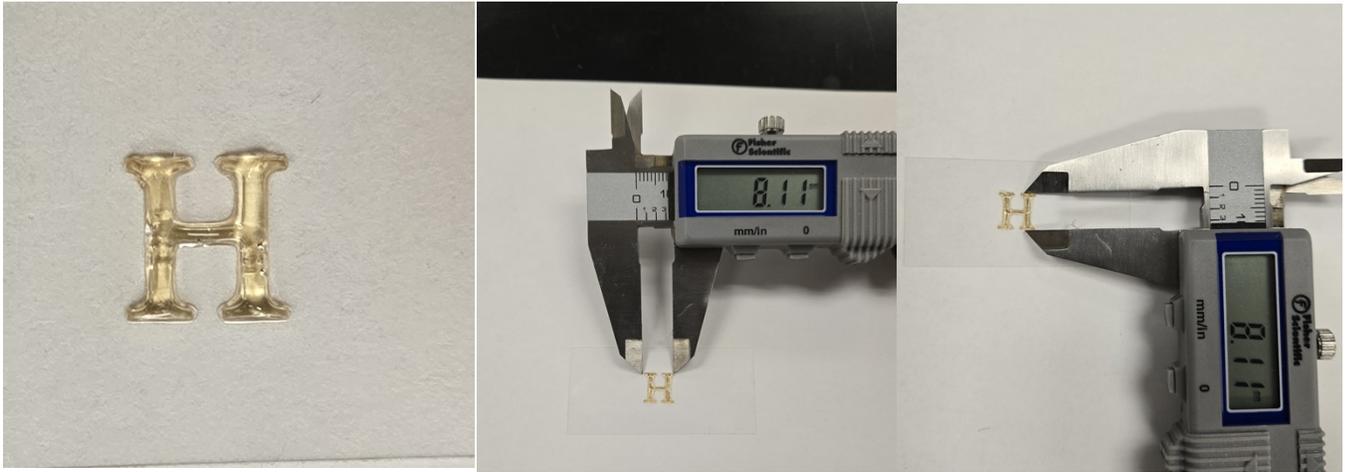


Step 5. Once the printing is complete, we remove the uncured resin by washing with ethanol.



The uncured resin can be reused.

Step 6. The above



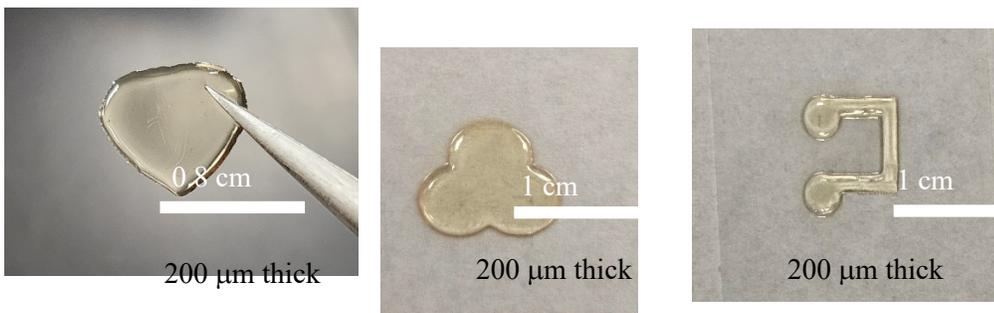
washed structure is further cured in a UV oven to get the final structure.

We note the fidelity of the structure in X and Y dimensions compared to the 3D model. We use a digital Vernier caliper, as shown, for measurement. In our pictures in the main text and this SI, we use a digital Vernier caliper to report an approximate scale based on such measurements. The height depends on the spacer.

S4. Additional examples of different printed structures

Centimeter-scale structures printed from the 80/20 ionic liquid photocurable mixture (labeled as 80/20 polymer) with the Halot Sky printer are presented below. Similarly, 1 wt. % of Au NPs in 80/20 ionic liquid photocurable (labeled as 1 wt. % of Au NPs) and 2 wt. % of Au NPs (labeled as 2 wt. % of Au NPs) in 80/20 ionic liquid photocurable. Scales and thickness are approximate and measured with a steel digital Vernier caliper micrometer.

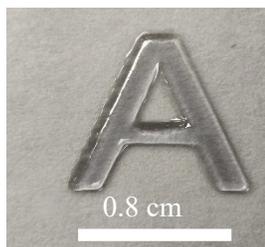
80/20 Polymer



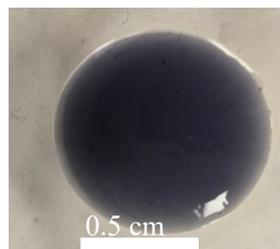
1 wt. % of Au NPs



500 μm thick

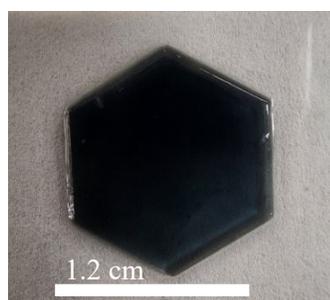


200 μm thick



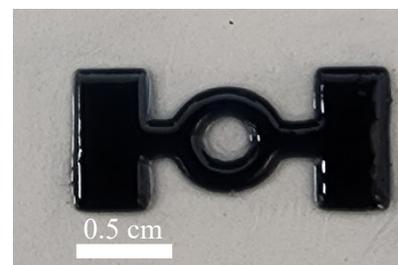
500 μm thick

2 wt. % of Au NPs



500 μm thick

500 μm thick



500 μm thick

Figure S7. 3D-UV centimeter-scale prints, both free-standing and adhering to glass substrate, are shown for various formulations. Scale bars are approximates.

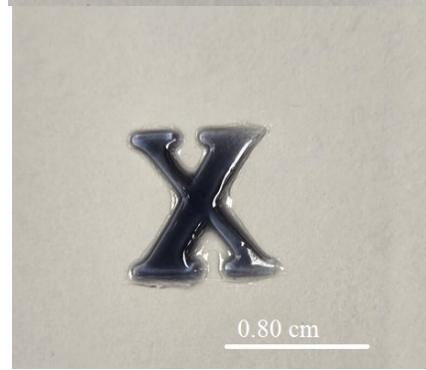
S5. Examples of printed structures with a different printer

Test structures were prepared with another LCD printer (405 nm, Photon Mono 4, Shenzhen Anycubic Technology Co., Ltd.). The legends are the same as previously described.

80/20 polymer



1 wt. % of Au NPs



2 wt. % of Au NPs

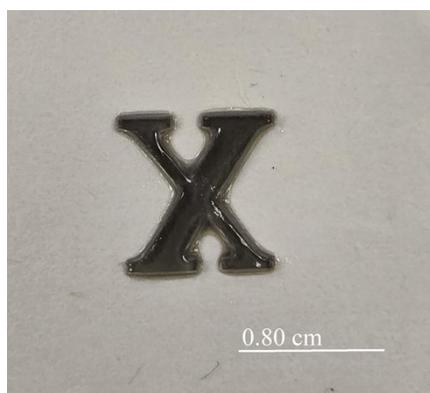
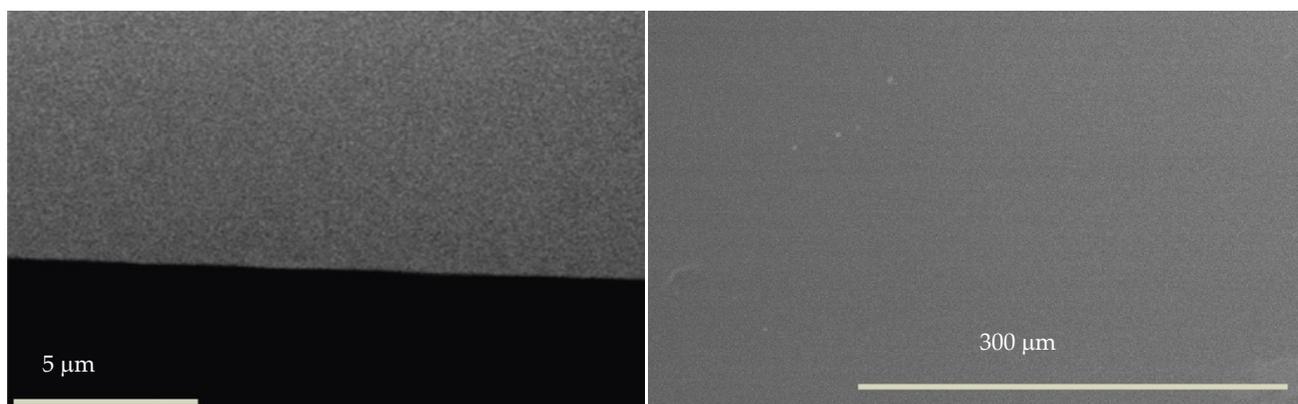


Figure S8. 3D-UV centimeter-scale prints adhering to a glass substrate are shown for various formulations. Scale bars are approximates.

S6. Additional examples of different SEM images

Printed structures from 80/20 ionic liquid photocurable mixture (labeled as 80/20 polymer), 1 wt. % of Au NPs in 80/20 ionic liquid photocurable (labeled as 1 wt. % of Au NPs) and 2 wt. % of Au NPs (labeled as 2 wt. % of Au NPs) in 80/20 ionic liquid photocurable are presented below.

80/20 polymer

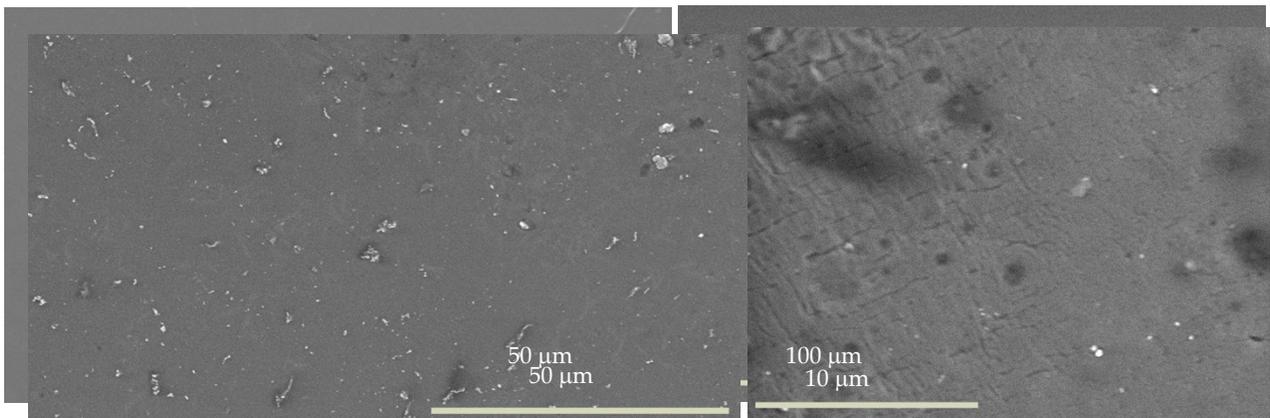


1 wt. % of Au NPs
2 wt. % of Au NPs

Figure S9. SEM images clearly show smooth surfaces for 3D-prints from 80/20 ionic liquid photocurable mixture and 1 wt. % of Au NPs in 80/20 ionic liquid photocurable mixture. Clumps, possibly from nanoparticles, are clearly visible in 2% formulations.

S7. Large area SEM image of a 3D-print with 1 wt. % of Au NPs in 80/20 ionic liquid photocurable resin

The figure below is a wide-area observation of a 3D-print of a structure using 1 wt. % of Au NPs in 80/20 ionic liquid photocurable resin. The SEM image was obtained by stitching several areas



using the Zigzag functionality in Hitachi software. Scattered clumps are seen, which may be an agglomeration of nanoparticles.

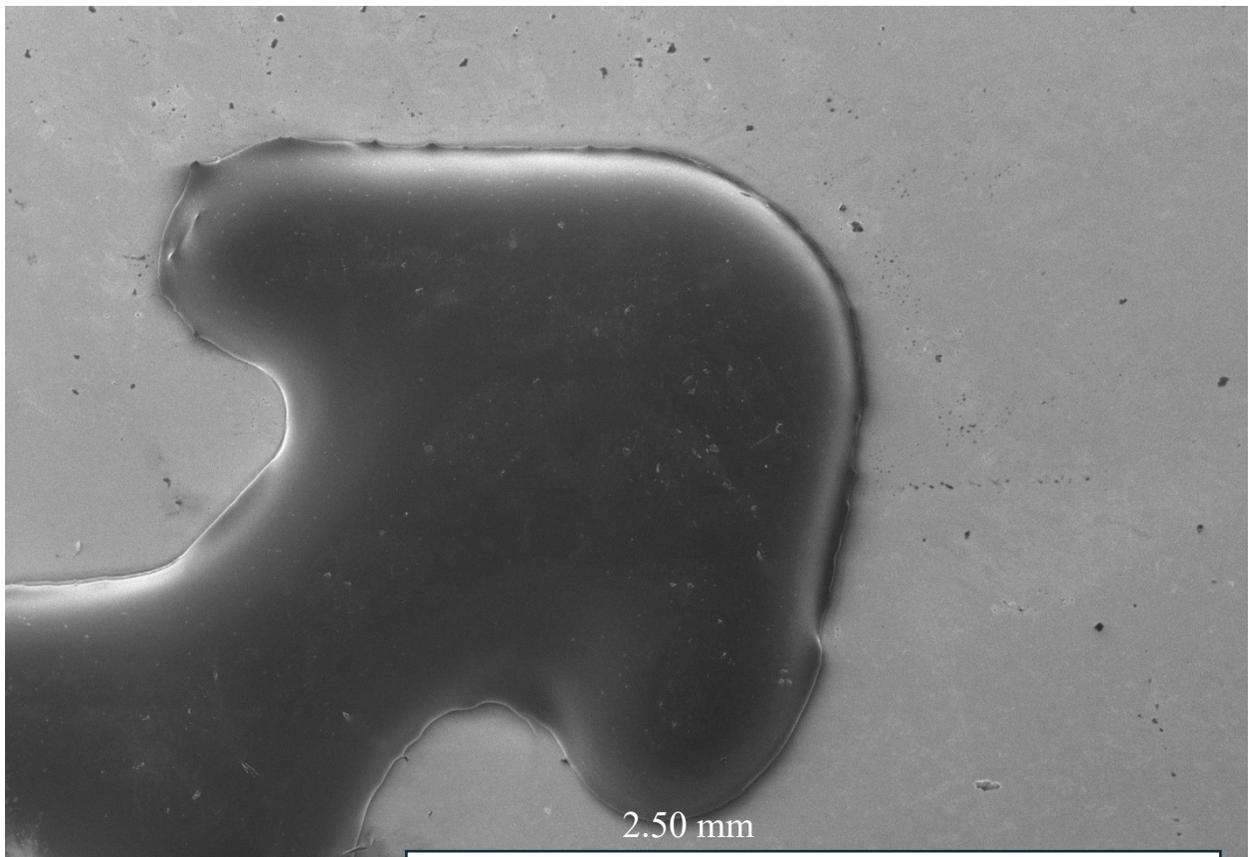
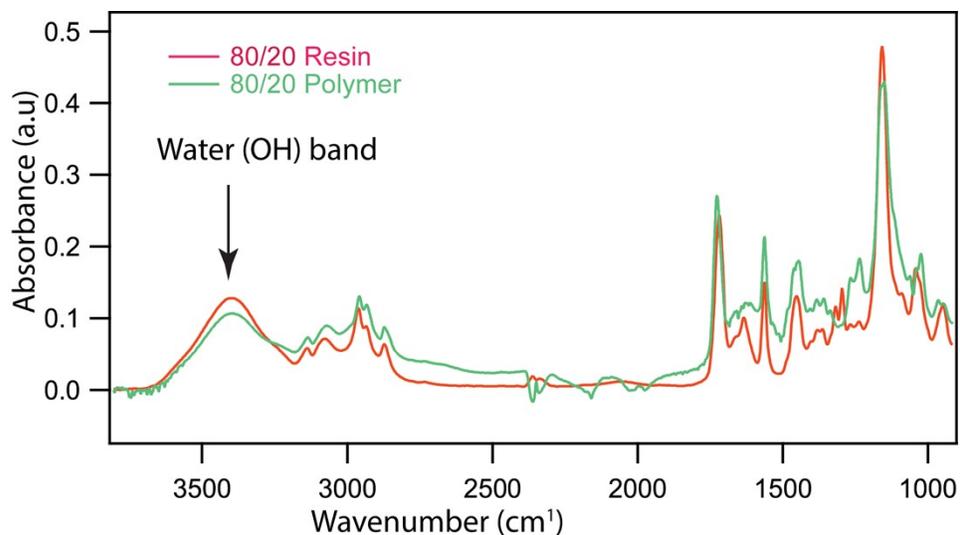


Figure S10. Large area SEM clearly shows smooth surfaces for 3D-prints from 1 wt. % of Au NPs in 80/20 ionic liquid photocurable formulation. .

S8. Additional spectra from infrared studies

The full spectrum of the liquid 80/20 ionic liquid photocurable mixture and its polymerized form is presented below. Notice the prominent H₂O stretching (O-H) modes around 3400 cm⁻¹. We see similar but lower intensity of OH stretching modes of polymerized ionic liquids with 1 wt. % of Au NPs in 80/20 ionic liquid photocurable and 2 wt. % of Au NPs in 80/20 ionic liquid photocurable, indicating lower water content with Au NPs embedded polymerized ionic liquids. Changes in the C-O band for polymerized ionic liquids with 1 wt. % of Au NPs in 80/20 ionic liquid photocurable and 2 wt. % of Au NPs in 80/20 ionic liquid photocurable is also presented.



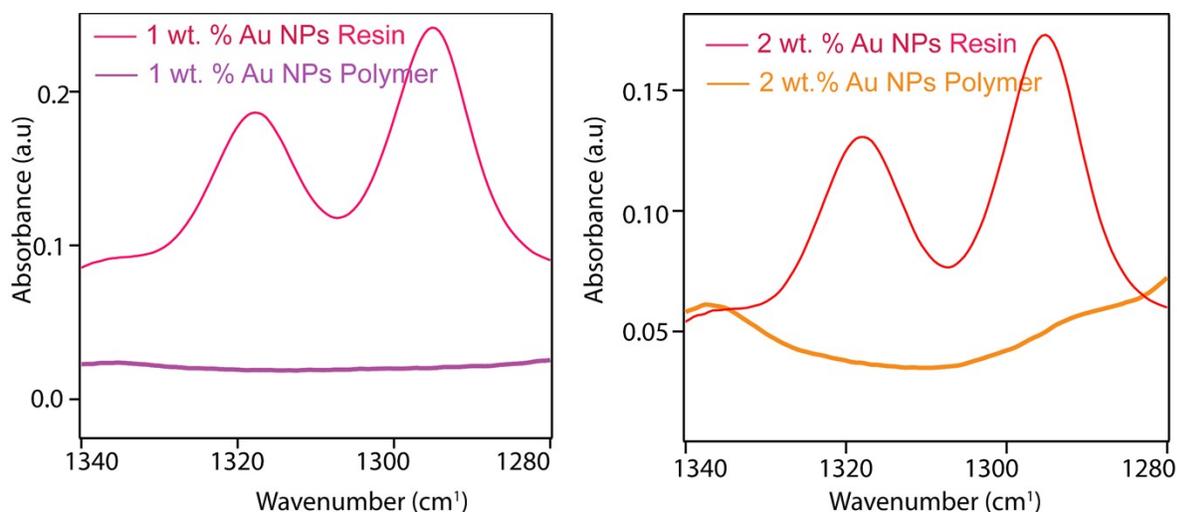


Figure S11. (Top) FTIR spectrum of 80/20 ionic liquid photocurable mixture (Red) and its polymerized form (Black). (Bottom) FTIR spectrum of C-O absorption region for polymerized 1 wt. % of Au NPs in 80/20 ionic liquid (Bottom, Left) and 2 wt. % of Au NPs in 80/20 ionic liquid (Bottom, Right) clearly shows the disappearance of the bands. Degree of polymerization is calculated from these changes.

S9. DSC results

Control experiments were performed with printed structures from 80 wt.% of the synthesized ionic liquid monomer and 20 wt.% of a commercial non-ionic crosslinker monomer, pentaerythritol tetramethacrylate. No T_g was found from the control prints. All other PILs T_g are given below along with their DSC thermograms.

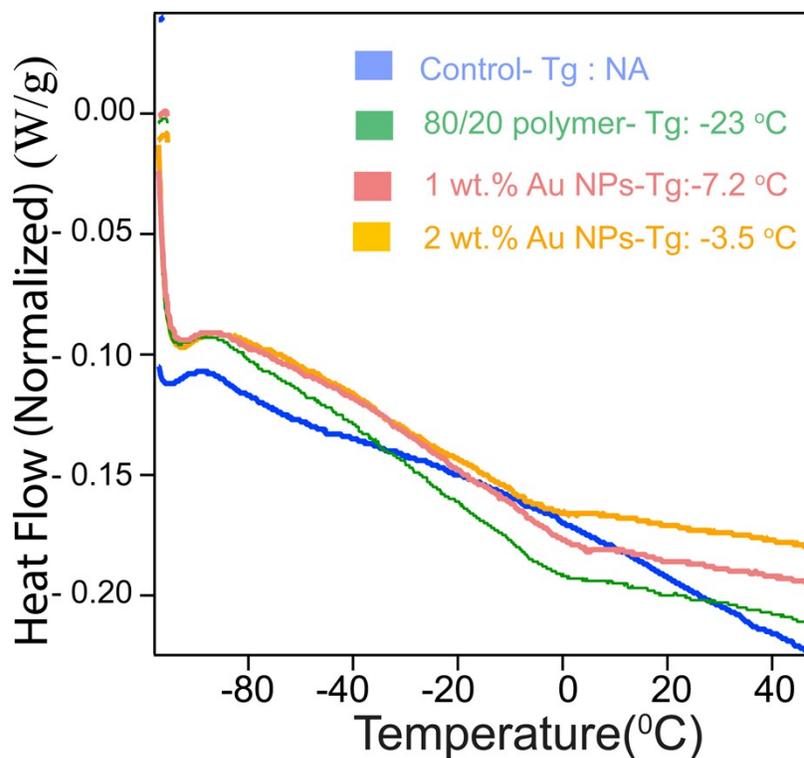


Figure S12. (Top) DSC thermograms reveal an increase in the glass transition temperature (T_g) with the addition of Au-NPs to the 80/20 ionic liquid photocurable mixture.

S10. Set-up for testing printed resistors

The schematics of the circuit diagram along with the actual arrangement is shown below. The variable DC power supply (Triplet Corp.) with an output of 30 V was used in the setup. A multimeter was used to measure the current. The printed resistor, as described in the main text, was connected via 34 B&S gauge nickel-chromium wire (Nichrome) or copper wires supported by alligator clips to the connector pad. Readings were taken every 20 minutes to study the stability of the circuit.

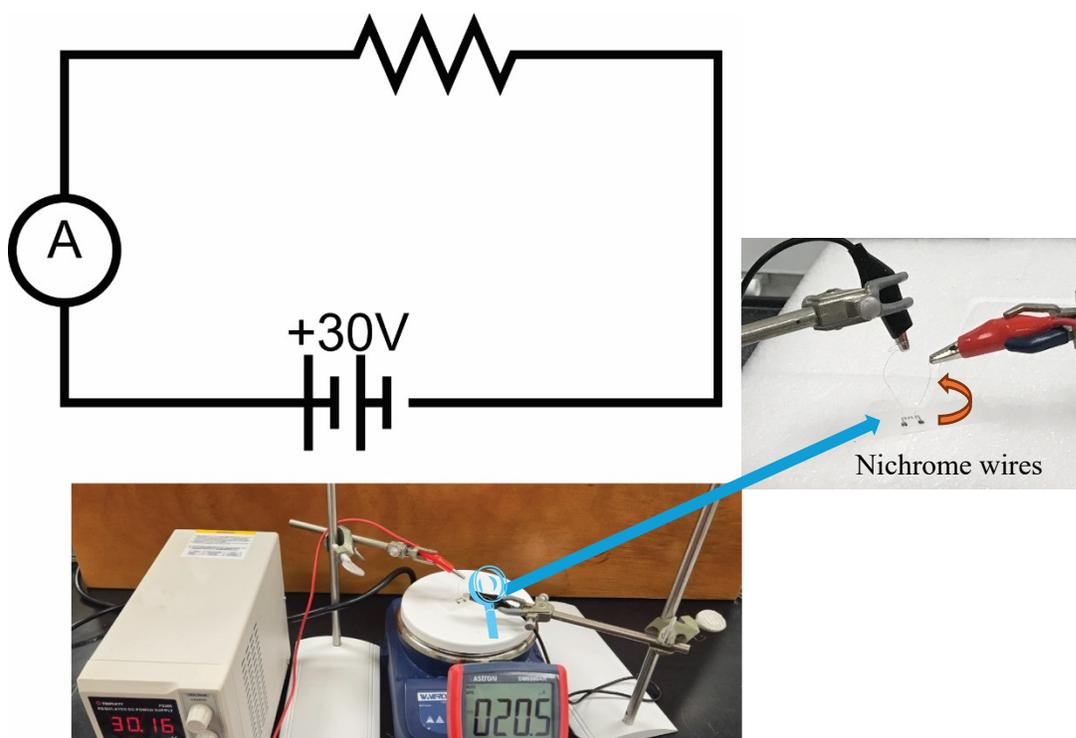


Figure S13. A test resistor printed from 1 wt. % of Au NPs in 80/20 photocurable ionic liquid clearly shows current in the microampere range. The magnifying glass shows a representative close-up of how the resistor is connected to the circuit. The current reading from the device is ~20 mA.