Electronic Supplementary Material (ESI) for ChemComm.

Molecular copper decomposition ink for printable electronics

Aaron Sheng,[‡,&] Abdullah Islam,[†,&] Saurabh Khuje,[†] Jian Yu,[£] Harvey Tsang,[£] Andres Bujanda,[£] and Shenqiang Ren[†,‡,#,*]

[‡] Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY, 14260, USA

[†] Department of Mechanical and Aerospace Engineering, University at Buffalo, The State University of New York, Buffalo, NY, 14260, USA

[#] Research and Education in Energy Environment & Water Institute, University at Buffalo, The State University of New York, Buffalo, NY, 14260, USA

[£] DEVCOM Army Research Laboratory, Aberdeen Proving Ground, MD, 21005, USA

[&] Equal contributions

shenren@buffalo.edu

Experimental

Materials. Copper(II) formate tetrahydrate (Cu-F), Diethylene glycol butyl ether (DEGBE), Dimethylformamide (DMF),), tetramethyl ethylenediamine (TMEDA), 2-amino-2-methyl propanol (AMP), ethylenediamine (EDA), butylamine (BA), octylamine (OA), triethylamine (TEA), aniline, hexadecylamine (HDA), dodecanoic acid (DDA), isopropanol (IPA)

Preparation of Cu-F MOD particles. The MOD complex was formed by complexing the respective ratios of Cu-F, DEGBE, and DMF within a ball milling grinding jar. A ratio of 4.5/5.0/0.45 was identified for optimal conductivity. The slurry was ball milled at 300 rpm for 1 hour after which the resulting ink was washed with DEGBE. The ink was washed by re-dispersing the solution within 2 mL of DEGBE with a vortex mixer. Excess solution was then poured off after centrifugation at 5000 rpm for 5 min. The ink was directly screen printed on Kapton with a 200 stainless steel mesh. After drying in open atmosphere, the prints were placed within a glass slide (Figure S7).

Preparation of Cu-A MOD Ink. The amines were first dissolved into an appropriate solvent to create an amine solution. Cu-F was then added into the amine solution changing the color to dark-blue or purple, indicating the Cu-F amine complex. This solution was then mixed until all the Cu-F was fully dissolved. The molar ratio of Cu-F to amines is 1:2. Initially, the solvent used was ethanol, then was changed to DI H_2O. Once dissolved, HPMC solution (2 wt.% HPMC in H_2O) was added to increase the viscosity of the ink. The final weight ratios are 1:1:2 (Cu-F amine complex: HPMC solution: H_2O). To assist with sintering, various amount of DDA (dissolved in IPA) were added.

First, the ink was applied through drop casting and allowing to dry. Later, direct writing was utilized through Voltera V-One for printing the MOD solutions onto plastics (Kapton®) and allowed to dry. Once dried, the prints were sintered under low nitrogen flow to remove any residuals while also decomposing the MOD into pure copper.

Characterization. Pre-sintered Cu-F inks and sintered films were studied with the use of a scanning electron microscope (SEM). The crystal structures of the Cu-F inks were characterized with a powder x-ray diffraction (pXRD) instrument. A thermogravimetric analysis was used to identify the decomposition of chemicals in solution.

Decomposition equation of copper formate

$$Cu(CHOO)_{2(g\ or\ aq)} \xrightarrow{\Delta} Cu_{(s)} + 2CO_{2(g)} + H_{2(g)} \qquad \text{(eq. 1)}$$

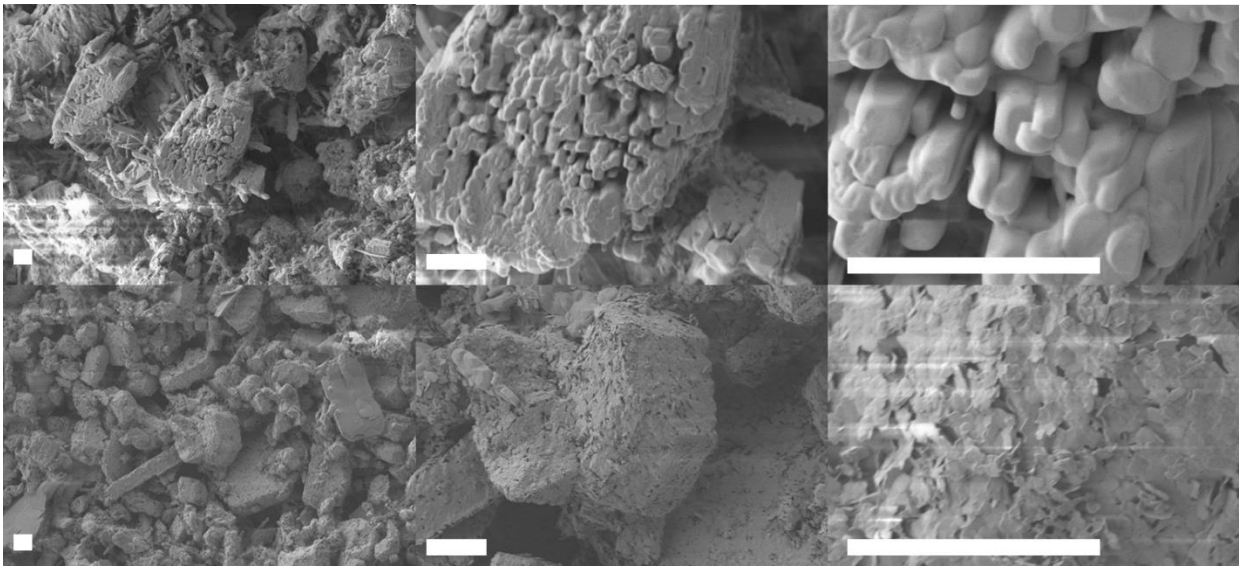

Figure S1. The SEM images of Cu-F particles that have been milled for (top) 30 and (bottom) 60 minutes. The SEM images show images which are zoomed in from left to right. The scale bar represents 5 μm.

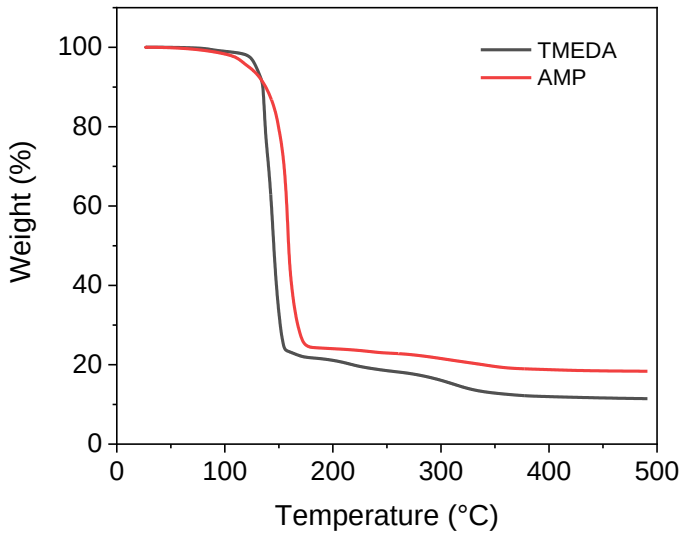

Figure S2. The TGA for Cu-F complexed with only TMEDA (black) and only AMP (red).

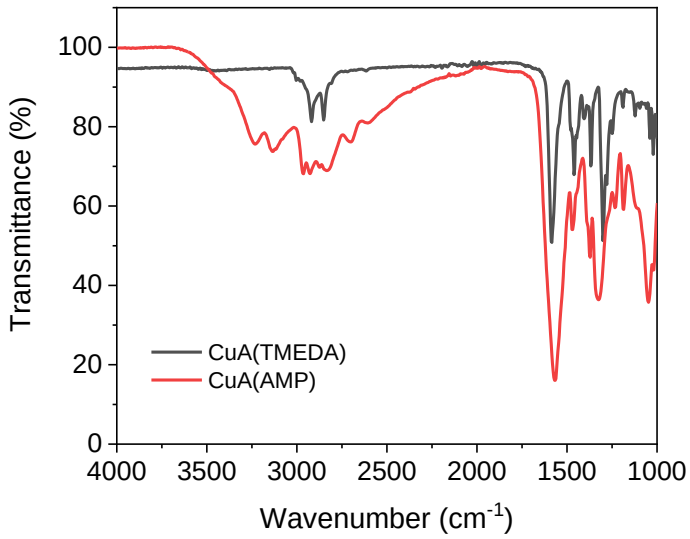

Figure S3. The FTIR spectrum of Cu-F TMEDA (black) and Cu-F AMP (red).

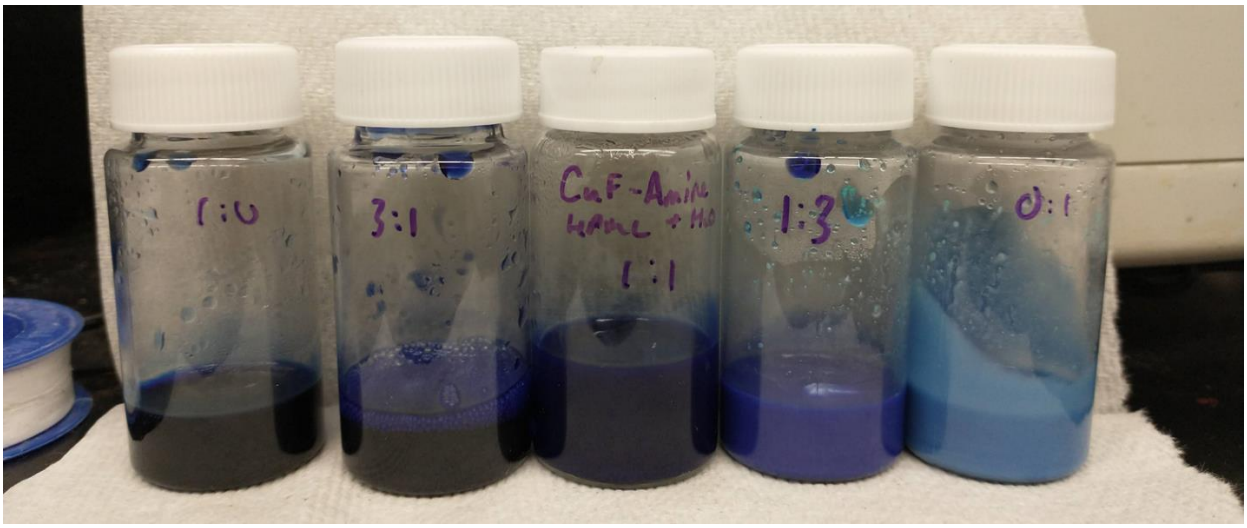

Figure S4. Cu-F amine inks at various amine ratios. The amines ratios here represent the molar ratio of TMEDA:AMP.

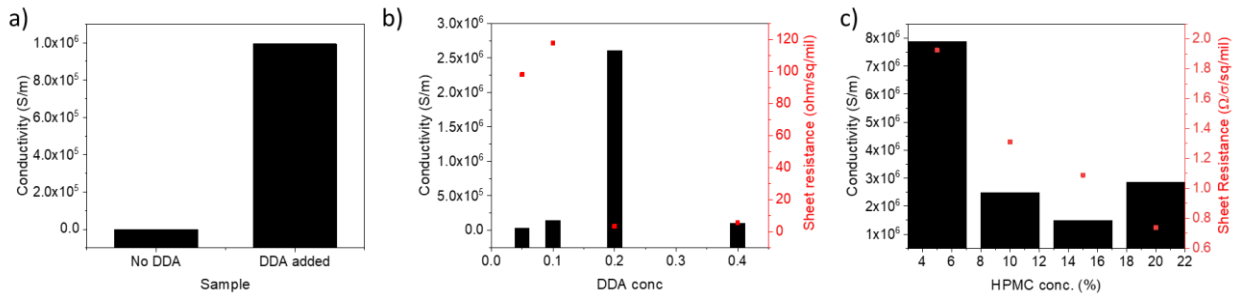

Figure S5. The conductivity (black) and sheet resistance (red) values of Cu-A MOD ink after sintering (a) with or without DDA addition , (b) DDA concentration, and (c) HPMC concentration.

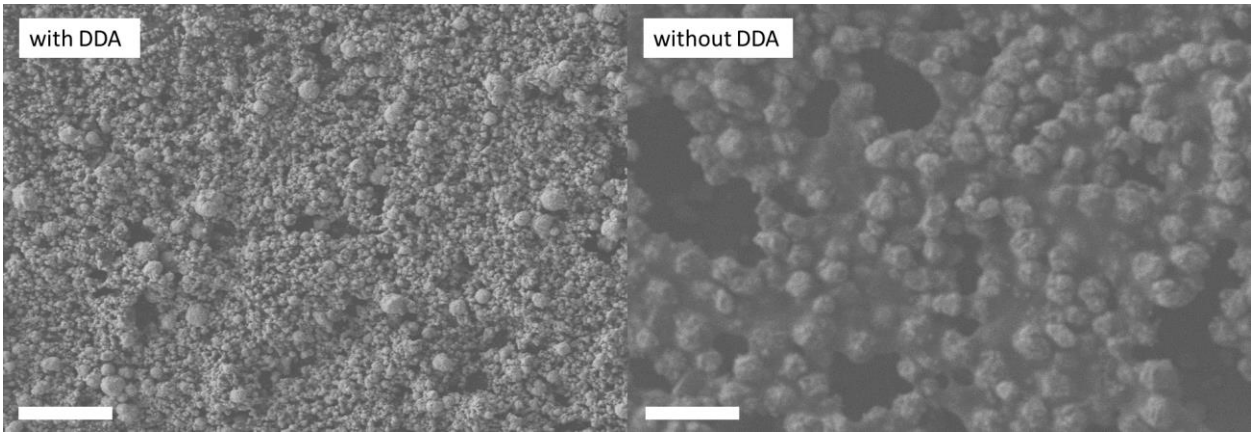

Figure S6. The SEM images of Cu-F amine inks sintered with (left) or without (right) the addition of DDA. The scale bar represents 5 μm.

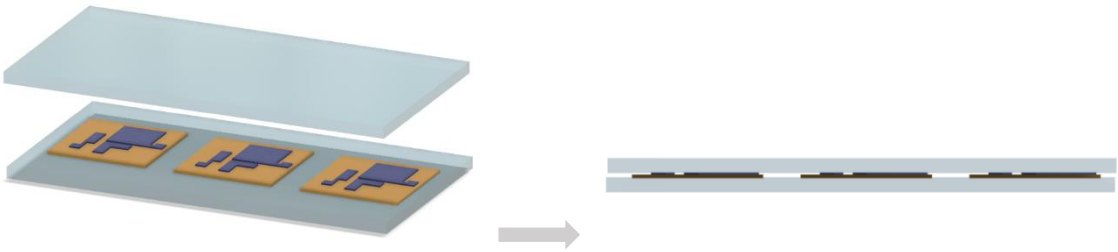

Figure S7. Schematic demonstrating samples sandwiched between two glass slides prior to sintering process.

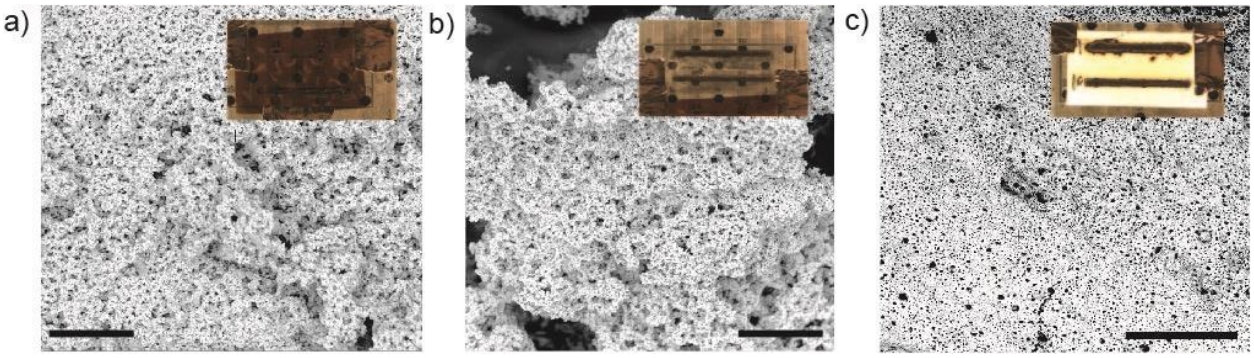

Figure S8. SEM images of Cu-F amine inks photonically sintered on Kapton (a), PET (b) and paper (c). Scale bars are sized to 30 μm, 30 μm and 80 μm respectively.

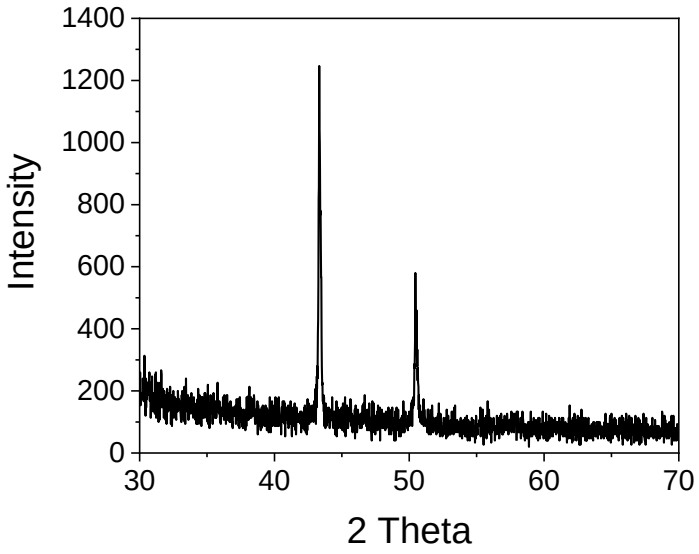

Figure S9. Powder XRD diffractogram of sintered samples.

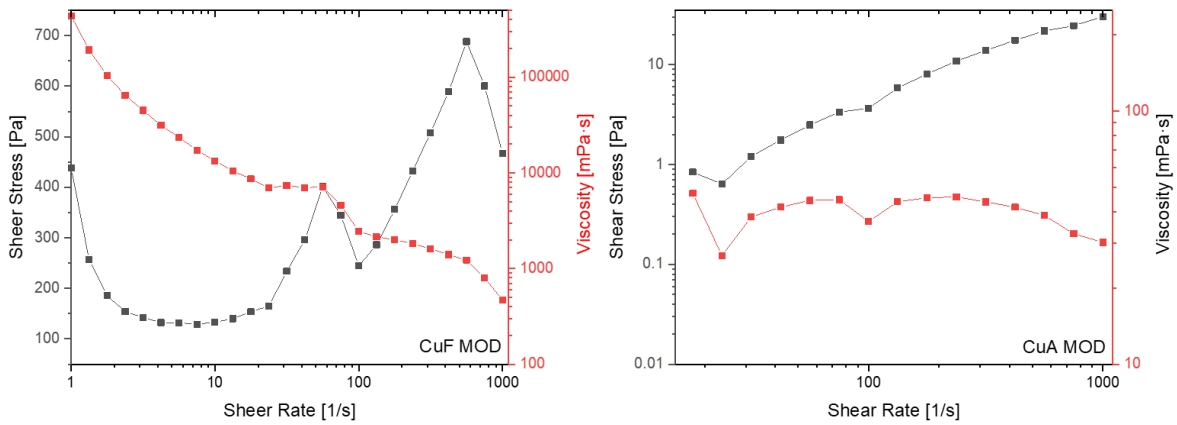

Figure S10. The viscosity and sheer stress dependence on the sheer rate applied on the Cu MOD ink.

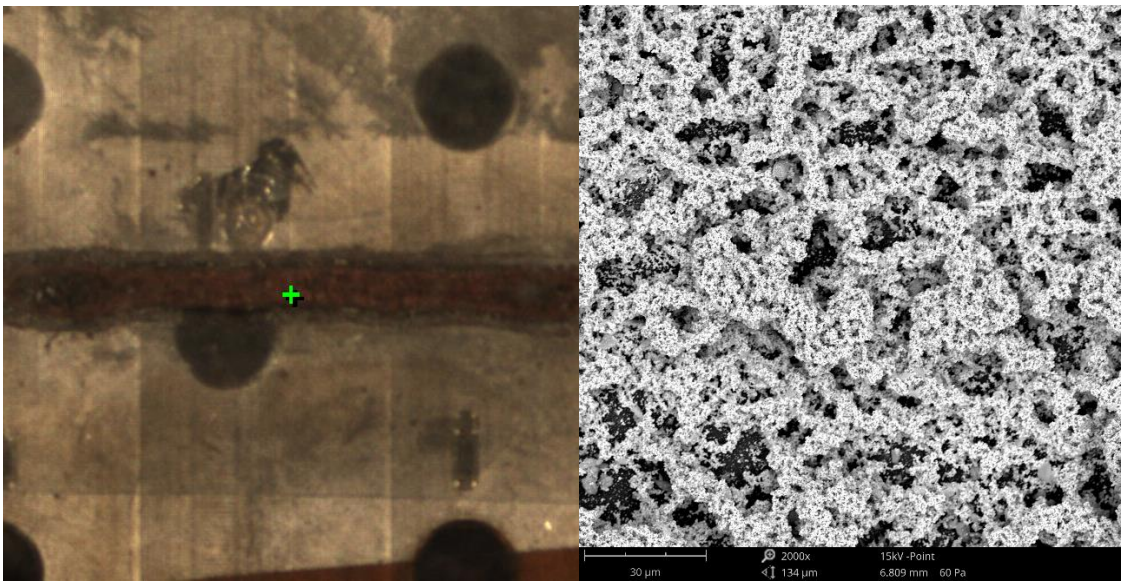

Figure S11. An optical image (left) and SEM image (right) of photonic sintered Cu MOD ink on PET.