

Supporting Information

Formulation of Screen-Printable Cu Molecular ink for Conductive/Flexible/Solderable Cu Traces

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Table S1. Overview of the reported conductive Cu inks.

Material	Organics	Binder	Adhesion	Mechanical test	Printing	Sintering Conditions	Volume Resistivity	Substrate	Ref.
CuNP Inks									
CuNP	Butoxyethoxy ethanol, 1-methoxy-2-propanol Glycerol	-	5B	2% strain Test fail > 130 bending cycles	Ink-Jet	130°C*	11 $\mu\Omega\cdot\text{cm}$	PET	11
						150°C*	7 $\mu\Omega\cdot\text{cm}$		
CuNP	ethanol	-	Nil	Nil	drop cast	250°C_N ₂	9 $\mu\Omega\cdot\text{cm}$	glass	12
Micro/nano Cu particle	propylene glycol, glycerol, antioxidant material	-	Nil	Nil	doctor-blade	Air 150°C	55 $\mu\Omega\cdot\text{cm}$	PI	14
						N ₂ _120°C	8.4 $\mu\Omega\cdot\text{cm}$		
						N ₂ _80°C	53 $\mu\Omega\cdot\text{cm}$		
Micro/nano Cu particle	propylene glycol, glycerol, 2-(2-butoxyethoxy) ethanol	-	5B	1000 cycle bending $\Delta R/R = 0.063$	bar-coater	N ₂ _150°C	50 $\mu\Omega\cdot\text{cm}$	PI, PET	15
						N ₂ _180°C	49 $\mu\Omega\cdot\text{cm}$		
						N ₂ _200°C	36 $\mu\Omega\cdot\text{cm}$		
CuNP	ethylene glycol	PVP	5B	Nil	Screen	IPL	28 $\mu\Omega\cdot\text{cm}$	PEN	35
							44 $\mu\Omega\cdot\text{cm}$	PET	
CuO NP Novacentrix			Nil	Nil	Inkjet	IPL	10 $\mu\Omega\cdot\text{cm}$	Silica coated PET	57
Cu MOD Inks									
Cu formate	2-amino-2-methyl propanol diethylene glycol methyl ether, pentanol, PVP, Luvitec K17	PVP	Nil	Nil	Inkjet	Plasma_N ₂	7.3 $\mu\Omega\cdot\text{cm}$	PEN, 3D-object	16
					Screen	Plasma_N ₂	-	PEN	
Cu formate	AMP, octylamine Carboxylic acid	-	Nil	Nil	Spin coating	N ₂ _350°C	9.5 $\mu\Omega\cdot\text{cm}$	glass	18
Cu formate	Monoiso-propanol amine, octylamine	PVP	Nil	5000 bending cycles R/Ro= ~30%	microplotter	N ₂ _140°C	20 $\mu\Omega\cdot\text{cm}$	glass, PI	19
Cu formate	isopropyl alcohol, hexylamine 2-amino-2-methyl-propanol	-	Nil	Nil	spin coating	Laser_N ₂	20 $\mu\Omega\cdot\text{cm}$	PI	20
						N ₂ _200-250°C	17 $\mu\Omega\cdot\text{cm}$		
Cu formate	AMP, octylamine isopropyl alcohol polyol solvents	APTES	Good adhesion Peel off test	R/R0 = ~10% at 2000 bending cycles	drop cast	Air 350°C	17 $\mu\Omega\cdot\text{cm}$	glass	21
Cu formate	primary and secondary amines, pyridines	-	Nil	Nil	tape mask	N ₂ _140-180°C	7-20 $\mu\Omega\cdot\text{cm}$	PI	28

Cu formate	DEAPD, DMAPD	-	Nil	Nil	doctor-blade	Air 180°C	300 μΩ.cm	glass	29
Cu neodecanoate + Cu(OH) ₂	terpineol	epoxy, ethyl cellulose, polyester resin	5B	Nil	screen	3% H ₂ 300-400°C	15-33 μΩ.cm	PI	36
Cu nitrate hydroxide	monosaccharides	-	Nil	Nil	screen	IPL	125 μΩ.cm	glass	38
Cu formate	2-amino-2-methyl-1 propanol	-	Nil	Nil	Inkjet	N ₂ 140°C	10.5 μΩ.cm	PET	40
Cu MOD + CuNP/Cu flake hybrid Inks									
Cu formate/ Cu particle	terpineol, dispersing agent	-	Nil	Nil	screen	Laser_N ₂	17 μΩ.cm	PI	37
						N ₂ 275°C	13 μΩ.cm		
Cu formate/ Sub-micron Cu particle** (37 wt% Cu)	2-amino-2-methyl-1 propanol	-	Nil	# R/R0 for PI= ~10% at 1000 inner bending cycles	doctor blade	N ₂ 140°C_ 10 min + Flash light	7.2 μΩ.cm	PI	42
		-					15.9 μΩ.cm	PEN	
		-					26.5 μΩ.cm	PET	
Cu formate/ CuNP (42 wt% Cu)	terpineol	-	5B	Nil	screen	N ₂ 250°C	8.2 μΩ.cm	PI	22
Cu formate/ Cu particle** (37 wt% Cu)	2-amino-2-methyl-1 propanol	-	Nil	Nil	screen	N ₂ 140°C	11.3 μΩ.cm	glass, PET	23
Cu formate /IPA/Cu (65 wt% Cu)	alkanol amine	-	Nil	Nil	doctor blade	N ₂ 100°C	900 μΩ.cm	alumina	24
Cu acetate/ Cu flake (55 wt% Cu)	Amino isopropanol	-	Nil	R/Ro= 4 at 1000 bending cycle	doctor blade	N ₂ 250°C	98 μΩ.cm	glass, PI	25
Cu(OH) ₂ / Cu formate/ Cu flake (30 wt% Cu)	diethylene glycol decanoic acid dodecanthiol	-	Nil	Nil	doctor blade	N ₂ 200°C	21 μΩ.cm	glass	27
					screen	-	-	PI	
Cu MOD + SWCNT/MWCNT Inks									
Cu Formate/ SWCNT	dipropylene glycol monomethyl ether, Disperbyk 180	PVP	Nil	Nil	Screen	IPL	0.106 S	PI	26
							-	PEN	
Cu formate/ MWCNT	2-amino-2-methyl-1 propanol/octylamine	-	Nil	*** R/R0 = ~40% at 10000 bending cycles	Screen	N ₂ 140°C	25.31 μΩ.cm	PET	39
aq Cu ion ink Cu(OH) ₂	NH ₄ OH, formic acid, citric acid	-	Nil	#R/R0 = >20% at 1000 bending cycles	rollerball pen sonoplot	IPL	3.1-5.27 μΩ.cm	PI/PET	41
* Sintered using formic acid ** > 50 wt % Cu amount in the hybrid ink is from Cu particles *** Bending test of Cu traces without MWCNT R/Ro = 400%. Centimeter scale features were printed. # PI= outer bending R/R0 > 20% at 200 cycle, PET and PEN= R/R0 > 20 % at 50 cycles									

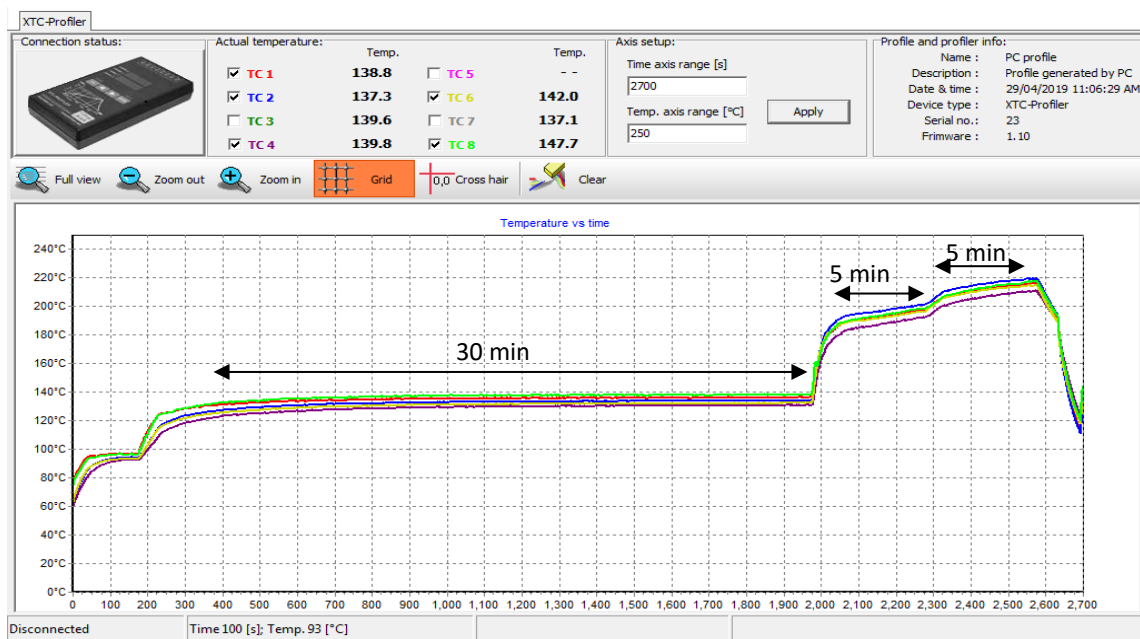


Figure S1. Data acquisition for thermal profile characterization on Kapton.

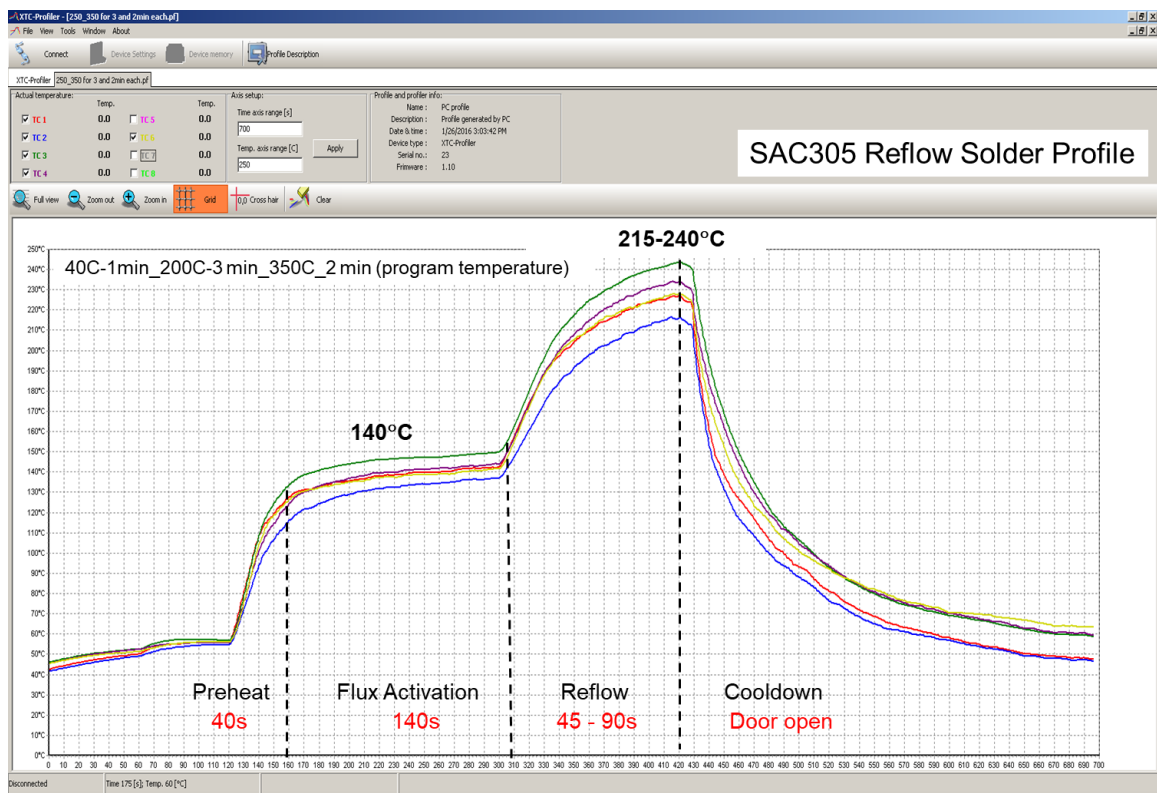


Figure S2. Reflow solder thermal profile of SAC305 solder paste on Kapton.

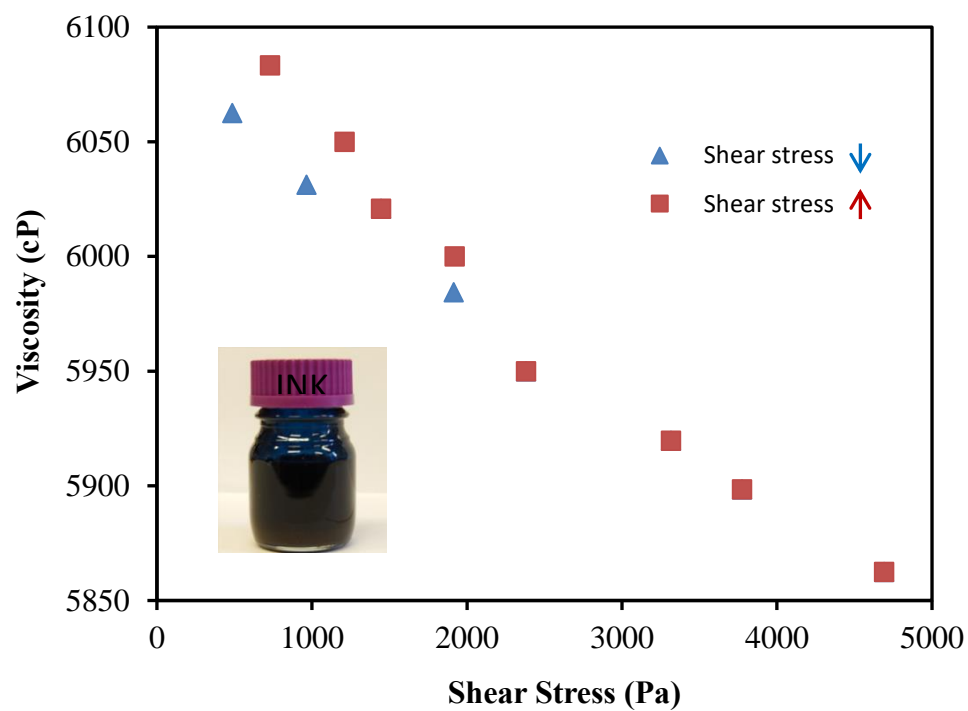


Figure S3. Rheological properties of the screen ink formulation, where it is shown to shear thin (viscosity decreases) when the shear rate (and shear stress) is increased (blue trace).

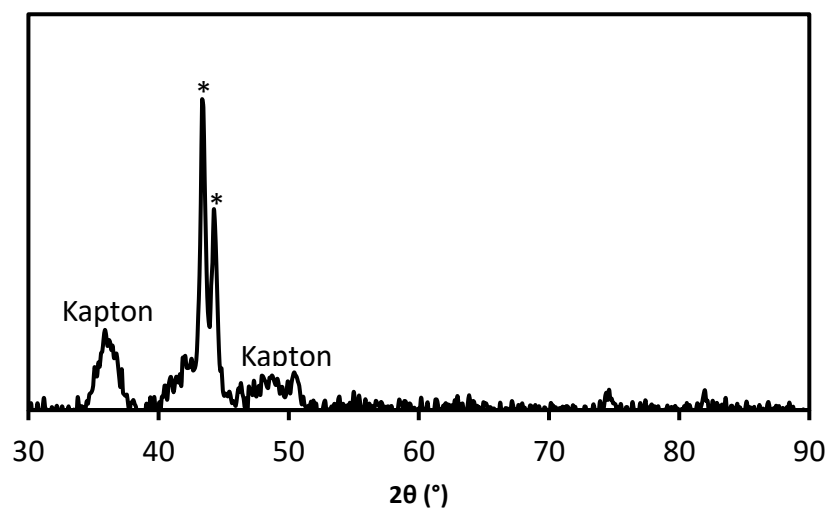


Figure S4. XRD of Kapton Substrate. The peaks denoted with asterisks (*) are attributed to the sample holder.

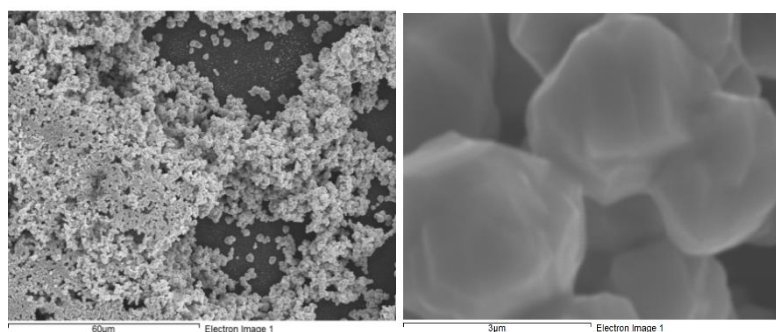


Figure S5. SEM's of screen printed trace sintered at $\sim 200^{\circ}\text{C}$ and $\sim 220^{\circ}\text{C}$ (substrate temperature) for 5 minutes each under nitrogen with 500 ppm oxygen.

Table S2. Comparison of physical and electrical data for linear 10 cm screen printed traces thermally and IPL sintered Cu molecular ink on Kapton™. Sintering conditions: ~130°C for 30 minutes to remove all solvent and subsequently sintered at ~ 200°C and ~220°C for 5 minutes (substrate temperature).

Sintering Method	Ink Formulation	Measured Linewidth (μm)	Resistance (Ω)	Sheet Resistance (mΩ/□)	Trace thickness (μm)	Sheet Resistivity (mΩ/□/mil)	Volume Resistivity (μΩ.cm)
Thermal	Cu MOD	517 ± 8	228 ± 22	1179 ± 30	1.75 ± 0.09	81 ± 2.2	206 ± 5.6
	Cu MOD + CuNP	528 ± 3	59 ± 3.5	310 ± 19	1.85 ± 0.10	23 ± 1.7	57 ± 4.3
	Cu MOD + Binder	525 ± 8	301 ± 17	1572 ± 103	1.7 ± 0.05	105 ± 4.5	267 ± 12
	Cu MOD + CuNP+ Binder	507 ± 16	123 ± 18	625 ± 92	1.31 ± 0.09	32.1 ± 2.3	81.5 ± 6.1
Photonic	Cu MOD	540 ± 9.8	100 ± 6.1	540 ± 0.1	1.1 ± 0.09	23 ± 2.7	60 ± 6.8
	Cu MOD + CuNP	527 ± 3.5	40 ± 0.8	206 ± 0.01	0.99 ± 0.09	8.2 ± 0.6	20 ± 1.8
	Cu MOD + Binder	531 ± 6.6	117 ± 6	623 ± 0.02	1.05 ± 0.08	26 ± 3.1	65 ± 7.8
	Cu MOD + CuNP+ Binder	545 ± 5.9	38.1 ± 1.7	213 ± 0.01	0.92 ± 0.05	7.7 ± 0.39	19.6 ± 1

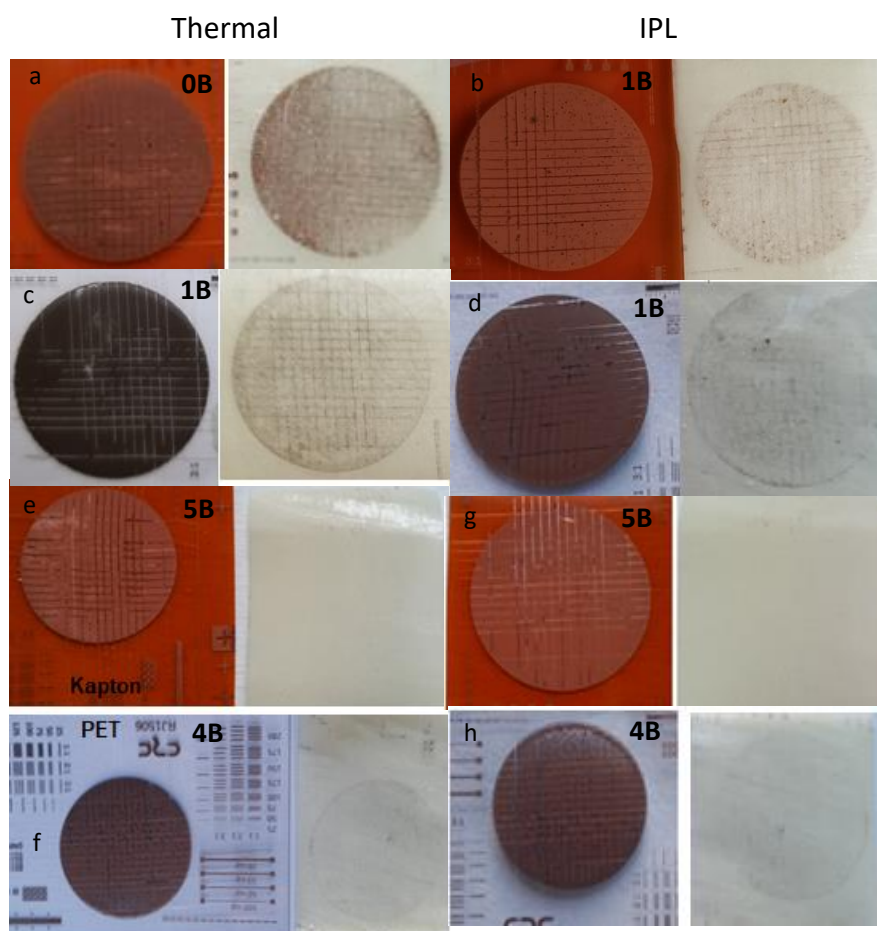


Figure S6. Adhesion of Cu traces thermally and IPL sintered on Kapton and PET without (a-d) and with (e-h) polyester binder. Adhesion was tested according to the ASTM D3359 standard, higher the grade better the adhesion 5B> 4B> 3B> 2B> 1B> 0B.

Table S3. ASTM F1683-02 flex and crease testing of IPL sintered traces produced from the molecular Cu ink on Kapton substrate.

		Measured trace widths (μm)					
		69 ± 0.8	105 ± 2.1	167 ± 1.3	305 ± 2	411 ± 6.2	545 ± 5.9
Compressive flex	% change in R	4.8 +/- 1.6	5.1 +/- 1.1	3.6 +/-1.3	3.0 +/- 1.5	4.8 +/- 1.6	4.1 +/- 1.6
	open fails	0/6	0/6	0/6	0/6	0/6	0/6
Tensile flex	% change in R	3.7 +/- 0.2	4.8 +/- 0.2	6.1 +/- 0.9	6.9 +/- 0.3	7.6 +/- 0.6	7.7 +/- 1.5
	open fails	0/6	0/6	0/6	0/6	0/6	0/6
Compressive crease	% change in R	2.7 +/- 1.2	3.5 +/- 1.7	3.2 +/- 0.6	5.8 +/- 0.9	6.8 +/-0.8	6.9 +/-0.8
	open fails	0/6	0/6	0/6	0/6	0/6	0/6
Tensile crease	% change in R	5.9 +/- 0.2	5.2 +/- 0.9	5.4 +/- 0.3	5.4 +/- 0.8	6.6 +/- 1.8	7.1 +/- 2
	open fails	0/6	0/6	0/6	0/6	0/6	0/6

Table S4. ASTM F1683-02 flex and crease testing of IPL sintered traces produced from the molecular Cu ink on PET substrate.

		Measured trace widths (μm)				
		77 ± 2.8	139 ± 0.7	240 ± 1.4	360.5 ± 0.7	467 ± 5.6
Compressive flex	% change in R	19.2 ± 1	18.7 ± 0.3	18.9 ± 1	18.1 ± 1.1	18.2 ± 0.4
	open fails	0/6	0/6	0/6	0/6	0/6
Tensile flex	% change in R	23.6 ± 1.3	24.1 ± 1.4	23.6 ± 0.8	23.4 ± 1.3	22.4 ± 0.6
	open fails	0/6	0/6	0/6	0/6	0/6
Compressive crease	% change in R	18.5 ± 3	19.6 ± 1.1	16.6 ± 2.5	17.2 ± 2.4	16.8 ± 2
	open fails	0/6	0/6	0/6	0/6	0/6
Tensile crease	% change in R	16.8 ± 3.1	16.8 ± 3.1	14.9 ± 0.9	15.2 ± 0.8	16.5 ± 0.8
	open fails	0/6	0/6	0/6	0/6	0/6

Table S5. ASTM F1683-02 flex and crease testing of thermally sintered traces produced from the molecular Cu ink on Kapton substrate.

		Measured trace widths (μm)					
		73 ± 3.9	97 ± 9	145 ± 14	262 ± 13	384 ± 17	507 ± 16
Compressive flex	% change in R	-	2.7 +/- 7	1.5 +/- 5	1.5 +/- 6	1.4 +/- 7	1.1 +/- 6
	open fails	5/5	0/5	0/5	0/5	0/5	0/5
Tensile flex	% change in R	-	91 +/-26	81 +/-16	91 +/- 7	99 +/- 11	100 +/- 2
	open fails	5/5	0/5	0/5	0/5	0/5	0/5
Compressive crease	% change in R	-	9 +/- 1.3	19 +/-3	16 +/- 0.6	19 +/- 3	19 +/- 4
	open fails	5/5	0/5	0/5	0/5	0/5	0/5
Tensile crease	% change in R	-	11 +/- 13	15 +/- 2	18 +/- 3	17 +/-5	16 +/-6
	open fails	5/5	0/5	0/5	0/5	0/5	0/5

Table S6. ASTM F1683-02 flex and crease testing of thermally sintered traces produced from the molecular Cu ink on PET substrate.

		Measured trace widths (μm)				
		102\pm 1.3	149 \pm 9.3	266 \pm 7.1	378 \pm 23	493 \pm 22
Compressive flex	% change in R	37.8 +/- 3.9	33.3 +/- 0.8	31.1+/- 3.7	31.5 +/- 2.5	29.4 +/- 1.5
	open fails	0/5	0/5	0/5	0/5	0/5
Tensile flex	% change in R	44.3 +/- 1.0	44.6 +/- 2.0	43.2 +/- 3.4	41.7 +/- 2.6	42.4 +/- 4.1
	open fails	0/5	0/5	0/5	0/5	0/5
Compressive crease	% change in R	34.4 +/- 1.4	32.1 +/- 1.8	30.6 +/- 2.7	30.8 +/- 1.1	29.4 +/- 0.9
	open fails	0/5	0/5	0/5	0/5	0/5
Tensile crease	% change in R	33.2 +/- 1.3	31.6 +/- 1.4	31.9 +/- 3.0	30.1 +/- 1.4	29.8 +/- 1.4
	open fails	0/5	0/5	0/5	0/5	0/5

Table S7. ASTM F1683-02 flex and crease testing of thermally sintered traces produced from the molecular Cu MOD ink with CuNP and without binder on Kapton substrate.

		Measured line widths (μm)					
		50.8	76.2	127	254	381	508
Compressive flex	% change in R	F	F	68 +/-18	59 +/- 11	46 +/- 4	46 +/- 7
	open fails	5/5	5/5	3/5	3/5	3/5	3/5
Tensile flex	% change in R	F	F	199+/- 16	197+/- 19	146 +/- 8	141 +/-5
	open fails	5/5	5/5	3/5	3/5	3/5	3/5
Compressive crease	% change in R	F	F	F	F	211 +/-3	205
	open fails	5/5	5/5	5/5	5/5	3/5	4/5
Tensile crease	% change in R	F	F	F	F	F	F
	open fails	5/5	5/5	5/5	5/5	5/5	5/5

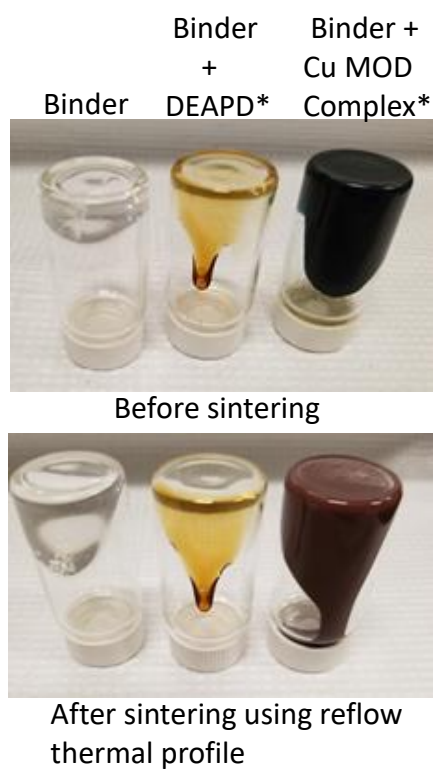


Figure S7: Fluidity test of binder dissolved in DEAPD and Cu MOD complex at higher temperature. *Binder used is 1 equivalent of DEAPD. Sintering thermal profile: $\sim 130^{\circ}\text{C}$ for 30 minutes then $\sim 200^{\circ}\text{C}$ and $\sim 220^{\circ}\text{C}$ for 5 minutes each (substrate temperature).

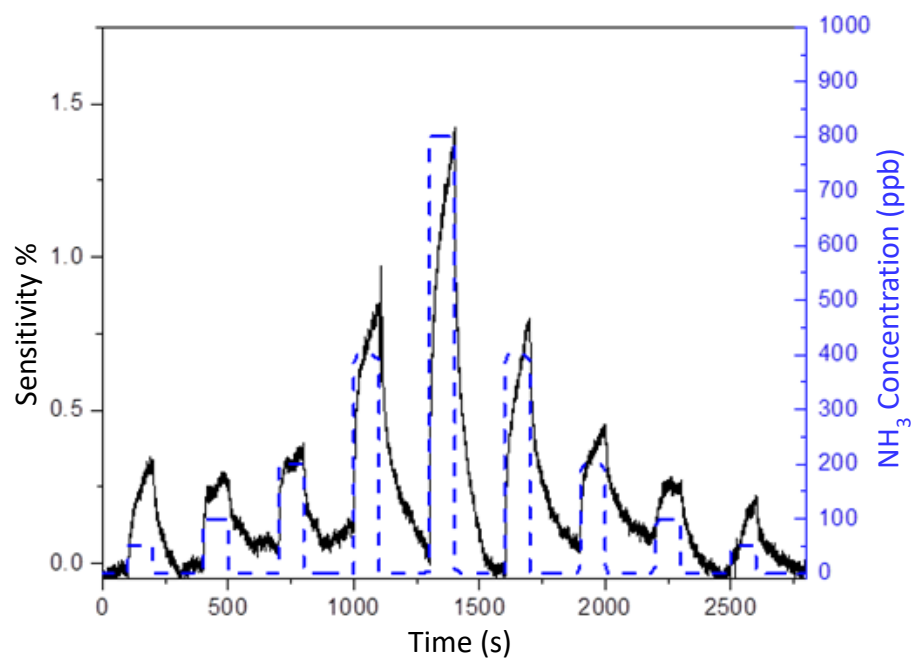


Figure S8. Response of screen printed Cu source-drain electrode on PFDD/SWCNTs TFTs to ammonia.