

Supporting Information

Mechanistic Insight into Bis(amino) Copper Formate Thermochemistry for Conductive Molecular Ink Design

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CONTENT

Figure S1. FTIR measurement of anhydrous copper formate vs. octylamine-copper-formate complexes.

Figure S2. Minimum energy configurations and energies upon formate rotation for bis(octylamine) copper formate: a) the reactant; b) TS; c) the product; d) the energy profile calculated by NEB method.

Figure S3. Minimum energy configurations and energies upon formate rotation for bis(3-butylpyridine) copper formate: a) the reactant; b)-e) 4 intermediate configurations with d) corresponding to TS; f) the product; g) the energy profile calculated by NEB method.

Figure S4. A schematic to describe the difference between “out-of-plane” and “in-plane” rotations that transform the O-bound to H-bound formate configuration.

Figure S5. Optimized structures and total energies of dimer compounds.

Figure S6. DSC-TGA-FTIR-MS curves of the thermolysis of bis(3,5-dimethylpiperidine) copper formate.

Figure S7. DSC-TGA-FTIR-MS curves of the thermolysis of bis(4-tertbutylpyridine) copper formate and bis(3-butylpyridine) copper formate.

Figure S8. ¹³C NMR of .a. Cu-OCT at 80°C for 1 hour b. Cu-PY at 90°C for 5 minutes.

Figure S9. ¹H NMR of a 1:1 mixture Cu(O₂CH)₂(C₈H₁₇NH₂)₂, and Cu(O₂CD)₂(C₈H₁₇NH₂)₂ heated to 90°C for 1 hour.

Figure S10. Optical microscopy images of the Cu₂OCT complex at various temperatures.

Scheme S1. Proposed pathways for intermolecular dihydrogen formation on Cu (II) formate amine compound.

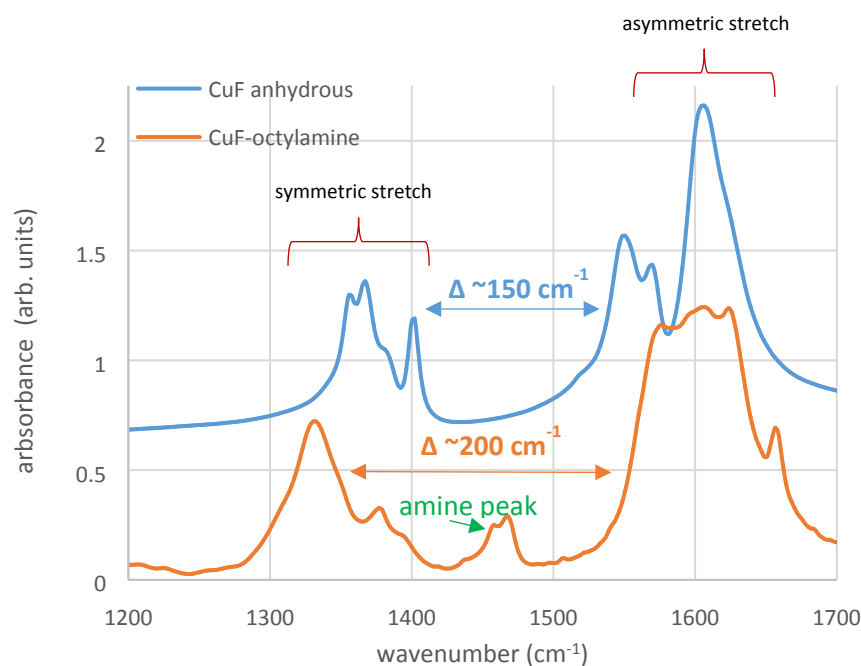


Figure S1. FTIR measurement of anhydrous copper formate vs. octylamine-copper-formate complexes: The asymmetric ($\sim 1600\text{ cm}^{-1}$) and symmetric ($\sim 1350\text{ cm}^{-1}$) carbon-oxygen stretching frequencies of the COO bonds of anhydrous copper formate and copper formate coordinated to octylamine. The geometry adopted between the copper center and COO⁻ will influence the carboxylate C-O bond lengths and O-C-O angle which in turn affects the wavenumbers of the symmetric (ν_{sym}) and antisymmetric (ν_{asym}) stretching frequencies. Low Δ values have been associated with formates bonded in a bridging (between two metals) or chelating geometries whereas high delta values have been linked to unidentate coordination between the formate and metal center due to their bonding geometries (refer to Deacon, G. B and Phillips, R. J., *Coord. Chem. Rev.* **1980**, 33, 227-250 and Sutton, C.C.R., da Silva, G. and Franks, G.V., *Chem. Eur. J.* **2015**, 21, 6801 – 680). The smaller separation between the two stretching frequency (Δ) of anhydrous copper formate suggests the formates form a connected network with formate bridging copper centers while copper formate coordinated to octylamine, with a higher Δ adopts unidentate coordination.

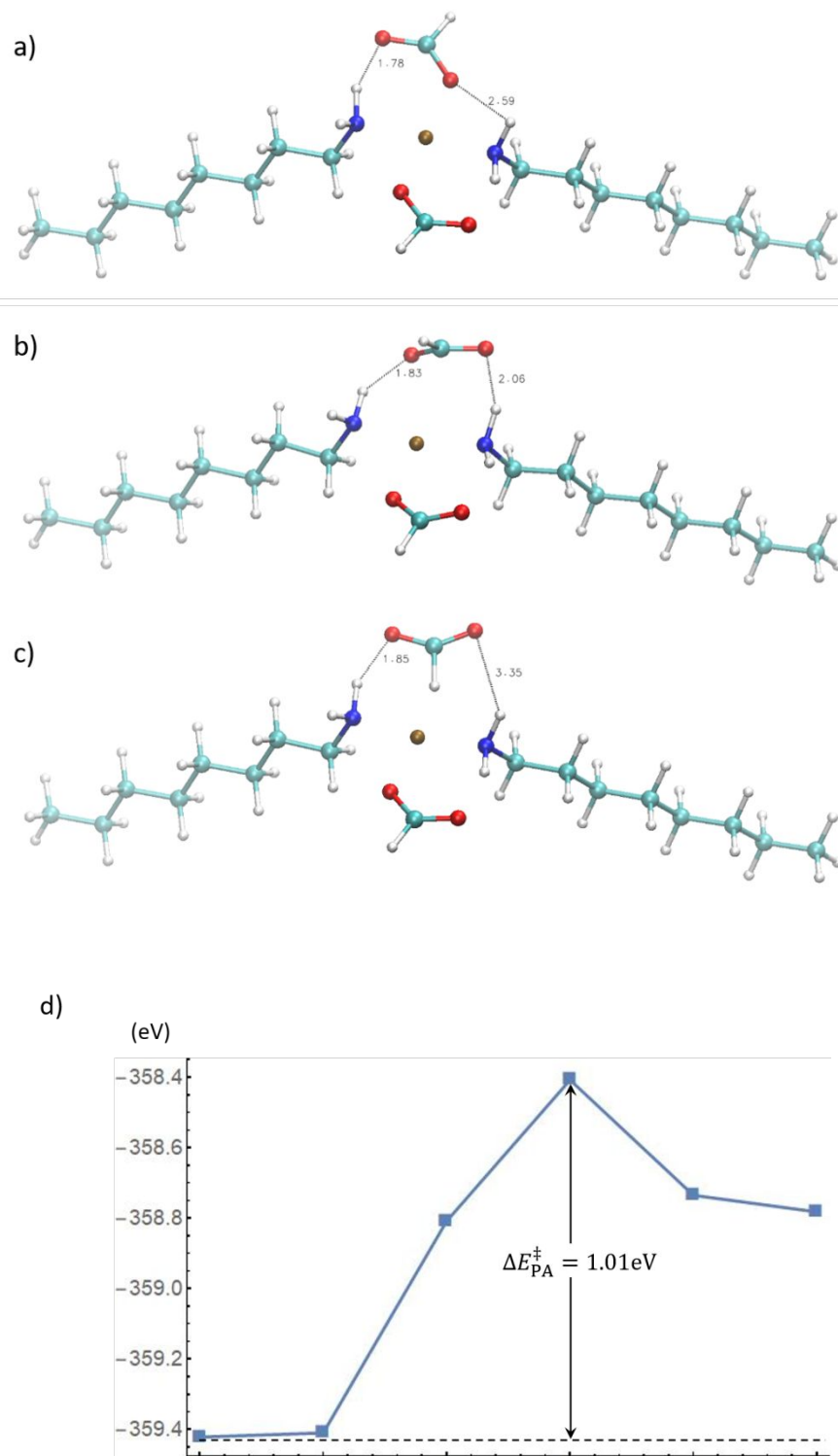


Figure S2. Minimum energy configurations and energies upon formate rotation for bis(octylamine) copper formate: a) the reactant; b) TS; c) the product; d) the energy profile calculated by NEB method.

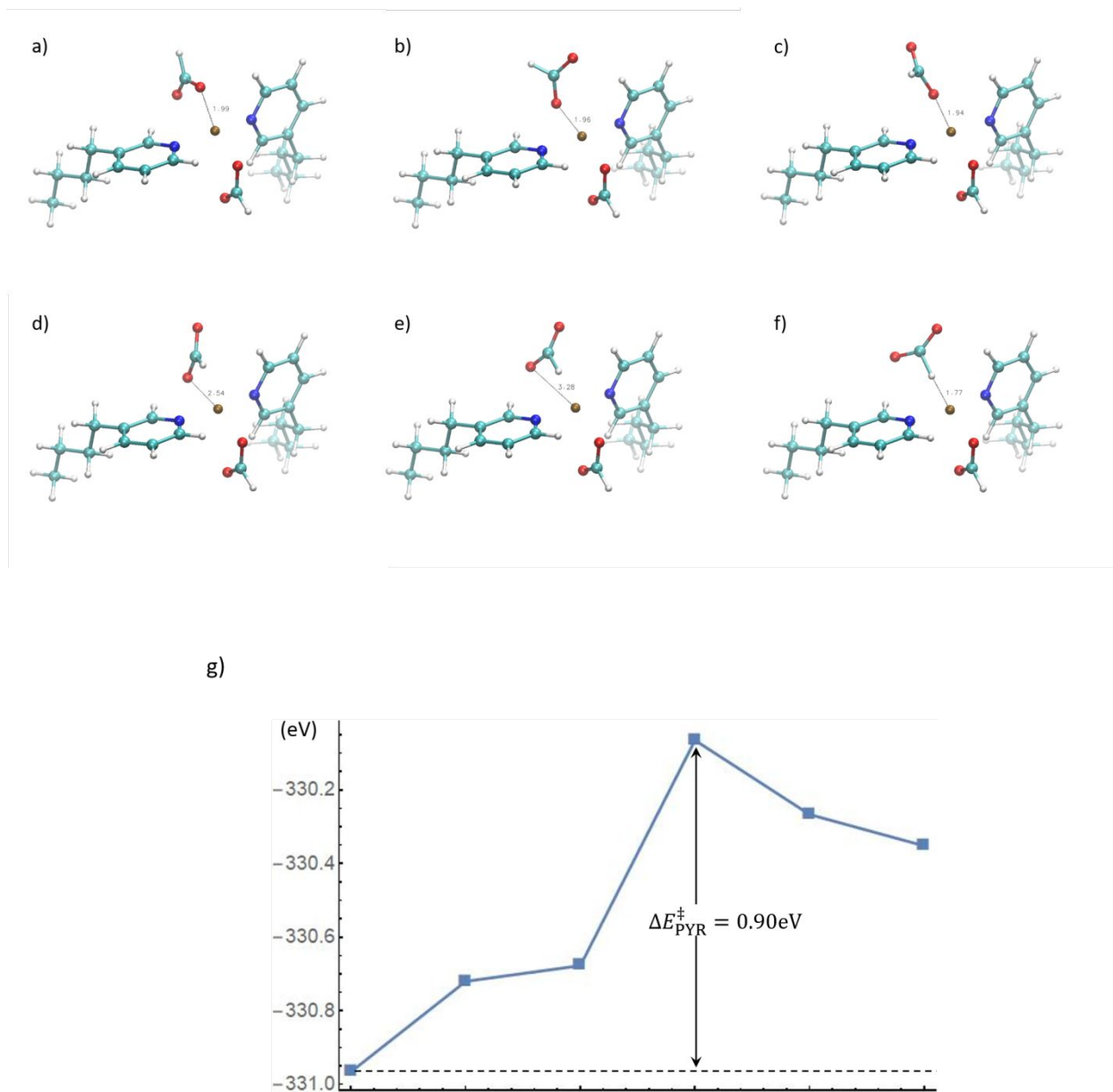


Figure S3. Minimum energy configurations and energies upon formate rotation for bis(3-butylpyridine) copper formate: a) the reactant; b)-e) 4 intermediate configurations with d) corresponding to TS; f) the product; g) the energy profile calculated by NEB method.

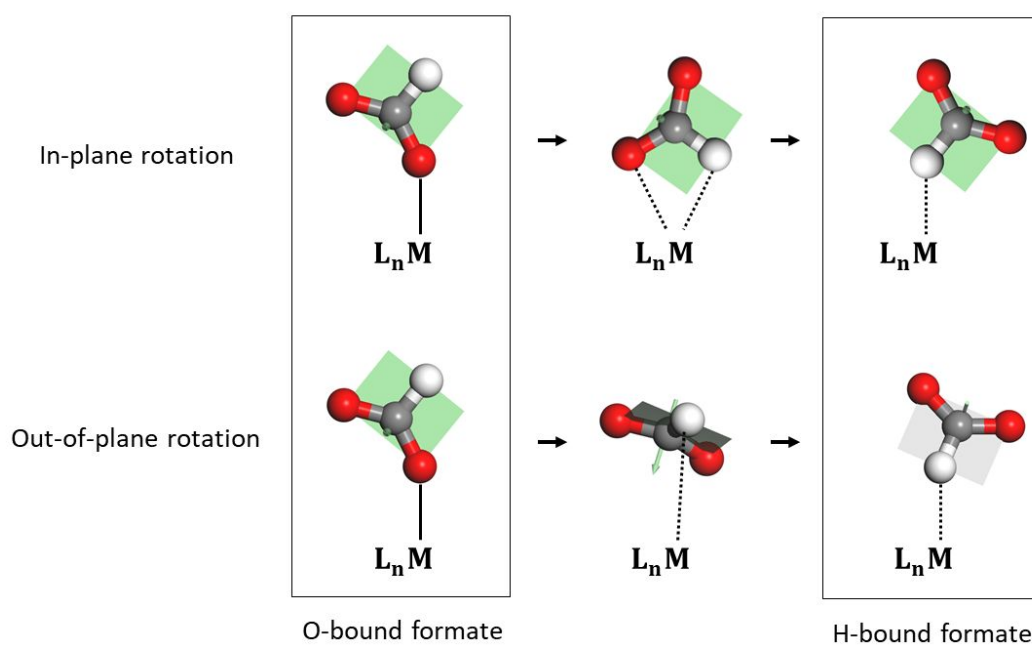


Figure S4. A schematic to describe the difference between “out-of-plane” and “in-plane” rotations that transform the O-bound to H-bound formate configuration.

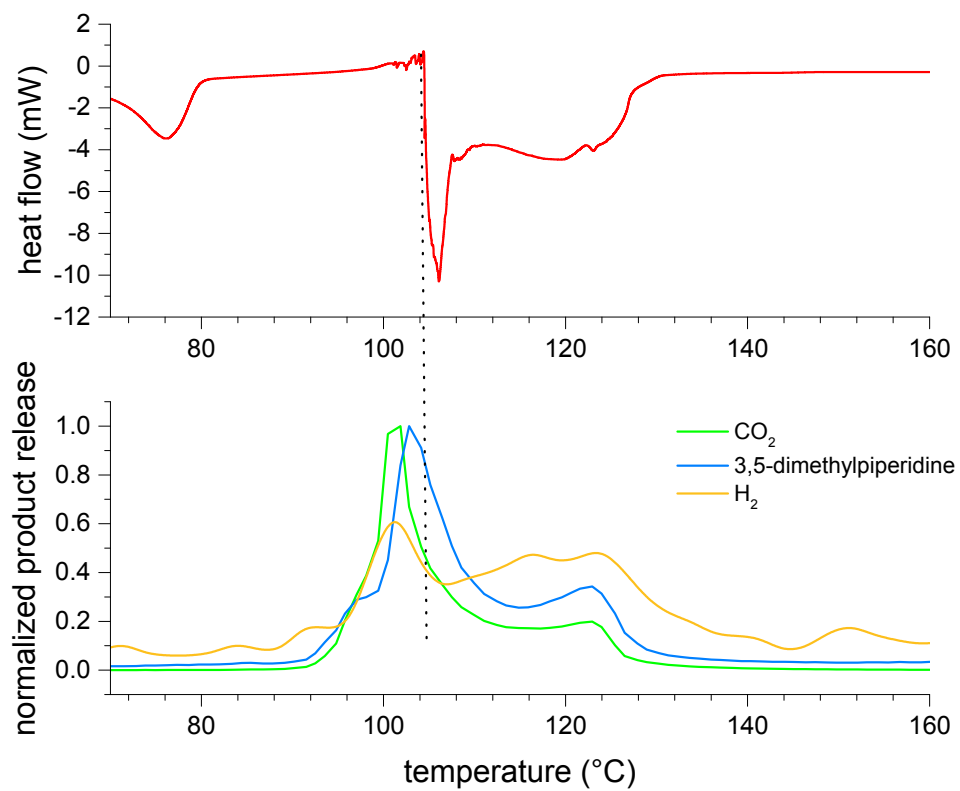


Figure S6. DSC-TGA-FTIR –MS curves of the thermolysis of bis(3,5-dimethylpiperidine) copper formate.

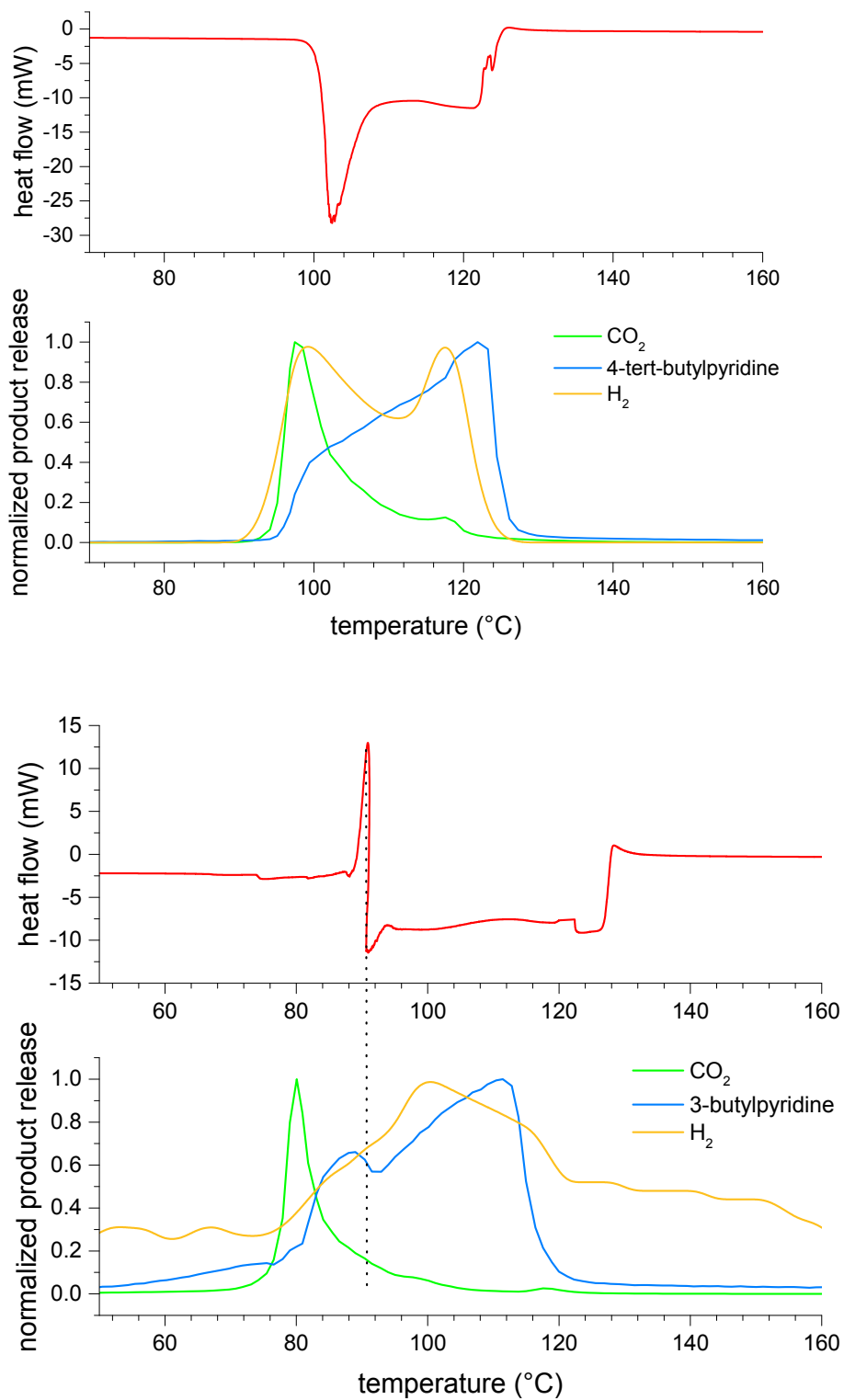


Figure S7. DSC-TGA-FTIR-MS curves of the thermolysis of bis(4-tertbutylpyridine) copper formate and bis(3-butylpyridine) copper formate.

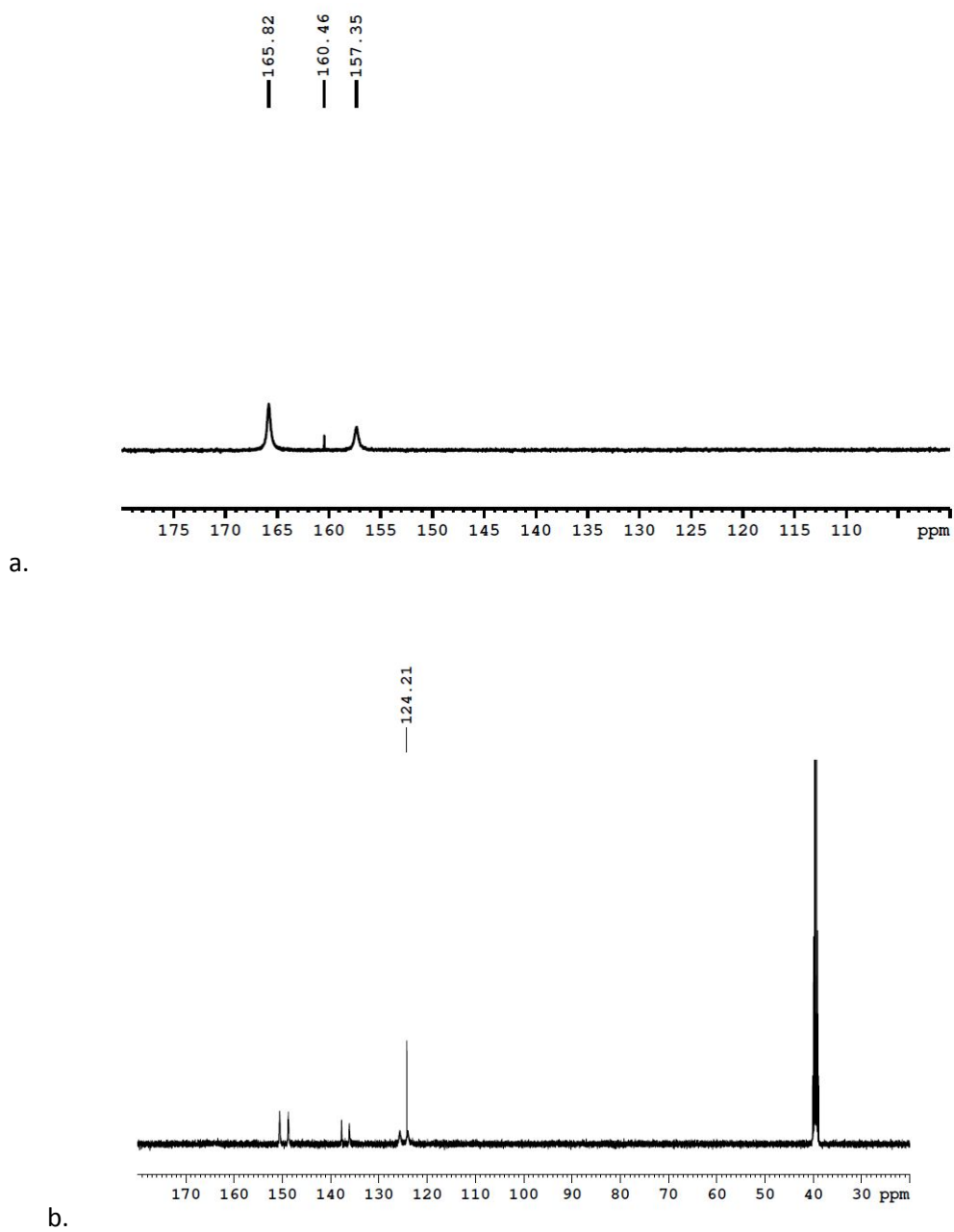


Figure S8. a) ^{13}C NMR of Cu-OCT heated to 80°C for 1 hour; b) ^{13}C NMR of Cu-PY heated at 90°C for 5 minutes.

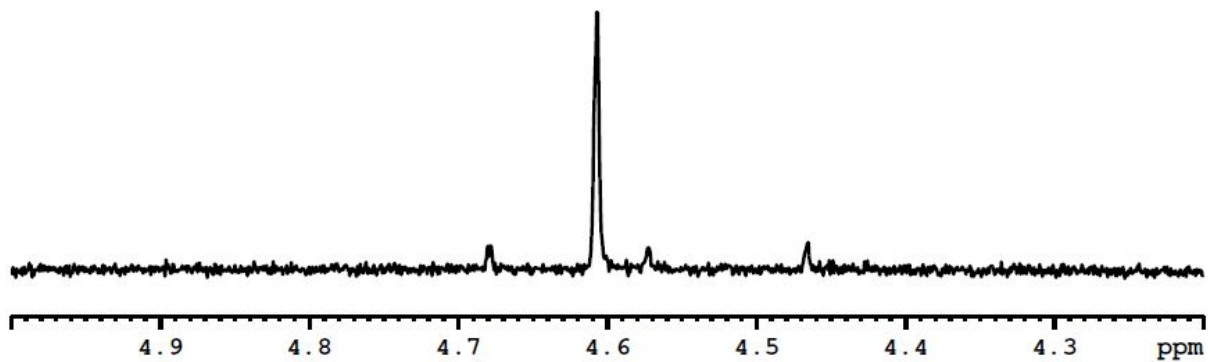


Figure S9. ¹H NMR of a 1:1 mixture $\text{Cu}(\text{O}_2\text{CH})_2(\text{C}_8\text{H}_{17}\text{NH}_2)_2$ and $\text{Cu}(\text{O}_2\text{CD})_2(\text{C}_8\text{H}_{17}\text{NH}_2)_2$ heated to 90°C for 35min, H₂:HD around 1:1 (mole ratio).

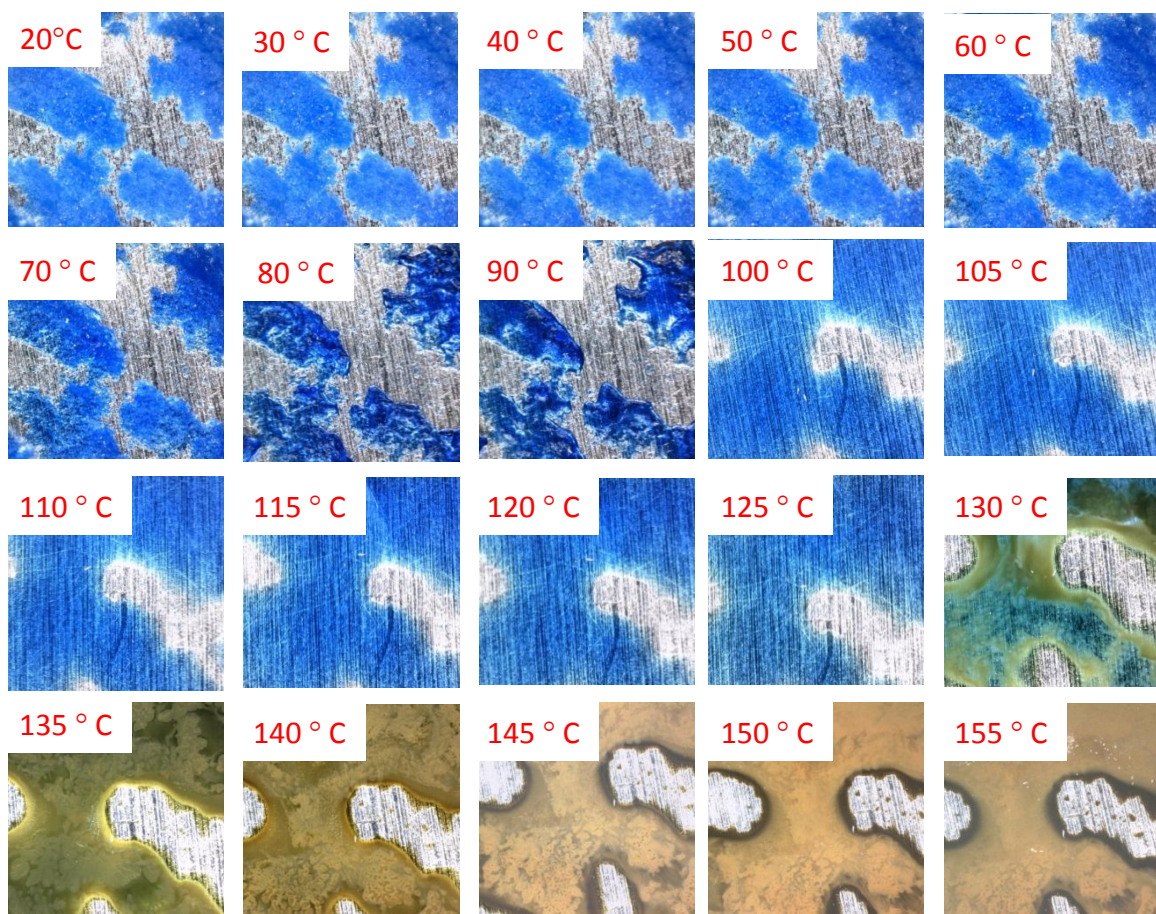
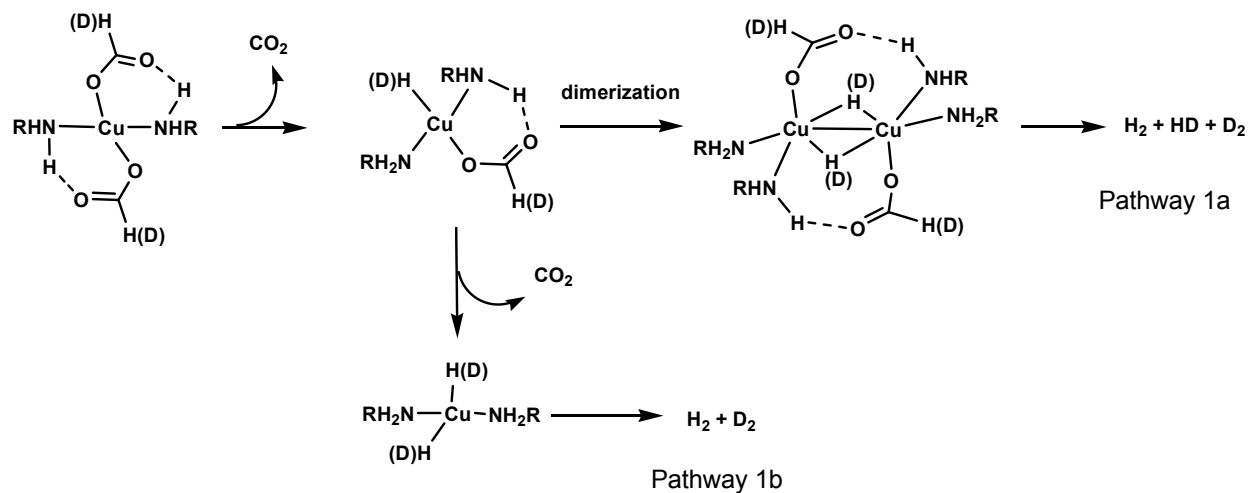


Figure S10. Optical microscopy images of the Cu_OCT complex at various temperatures. Phase transitions are present near ~80-90°C and 90-100°C. Note that the temperature between the above images and the DSC curves in the manuscript do not align exactly due to differences in the heating rates.



Scheme S1. Proposed pathways for intra and inter-molecular dihydrogen formation on CuOCT and Cu-OCT_D compounds. Pathway 1a describes the dimerization of copper formate to generated hydrogen inter-molecularly and yields H_2 , HD and D_2 when a 1:1 mixture of Cu-OCT and Cu-OCT_D is heated to 90°C , while Pathway 1b that describes the formation of hydrogen though an intramolecular process would generate H_2 and D_2 only.