

# Supporting Information

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

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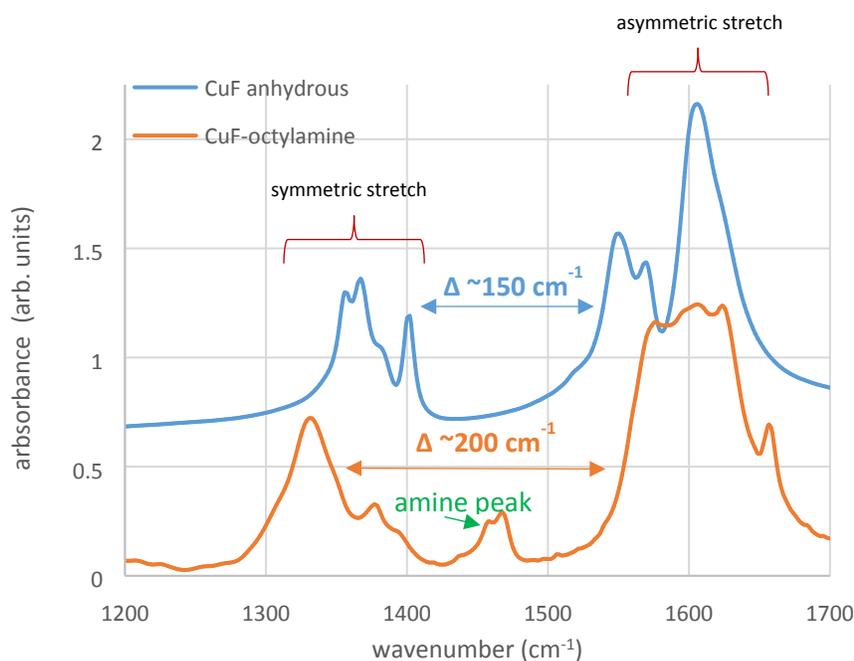
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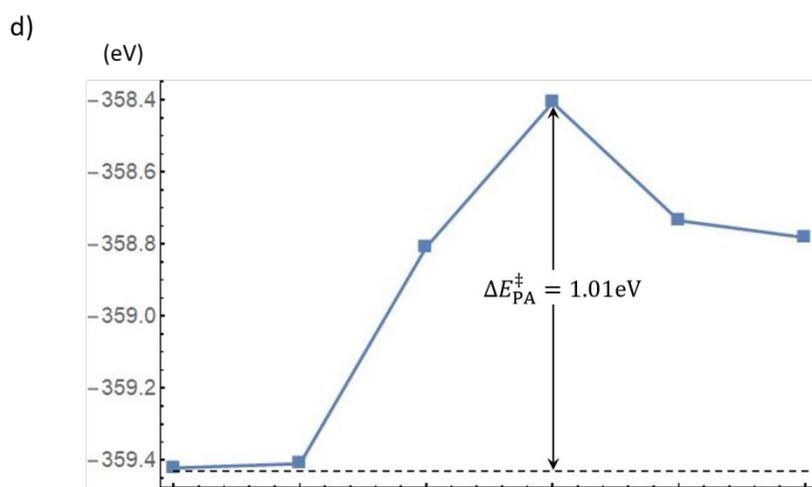
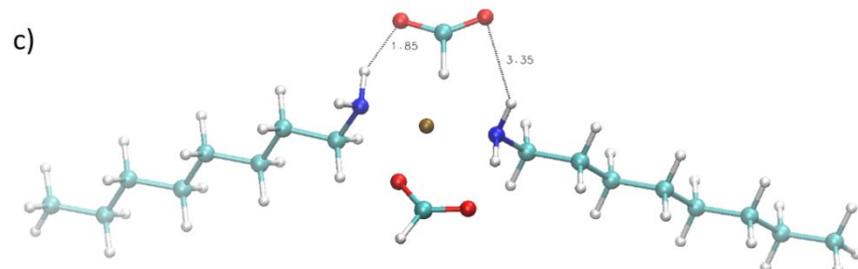
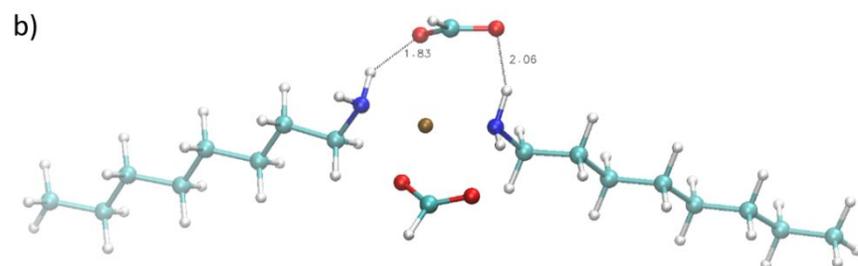
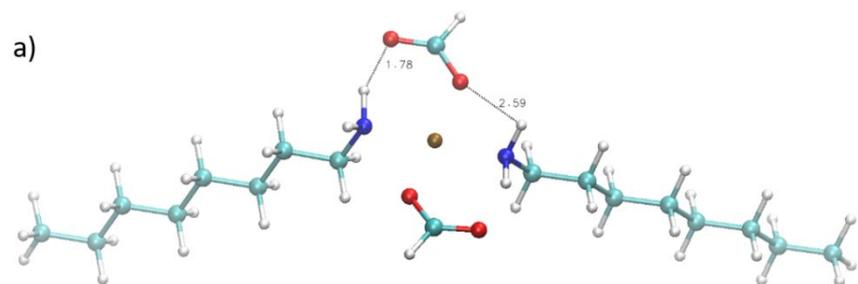
**Figure S9.** <sup>1</sup>H NMR of a 1:1 mixture Cu(O<sub>2</sub>CH)<sub>2</sub>(C<sub>8</sub>H<sub>17</sub>NH<sub>2</sub>)<sub>2</sub>, and Cu(O<sub>2</sub>CD)<sub>2</sub>(C<sub>8</sub>H<sub>17</sub>NH<sub>2</sub>)<sub>2</sub> heated to 90°C for 1 hour.

**Figure S10.** Optical microscopy images of the Cu\_OCT complex at various temperatures.

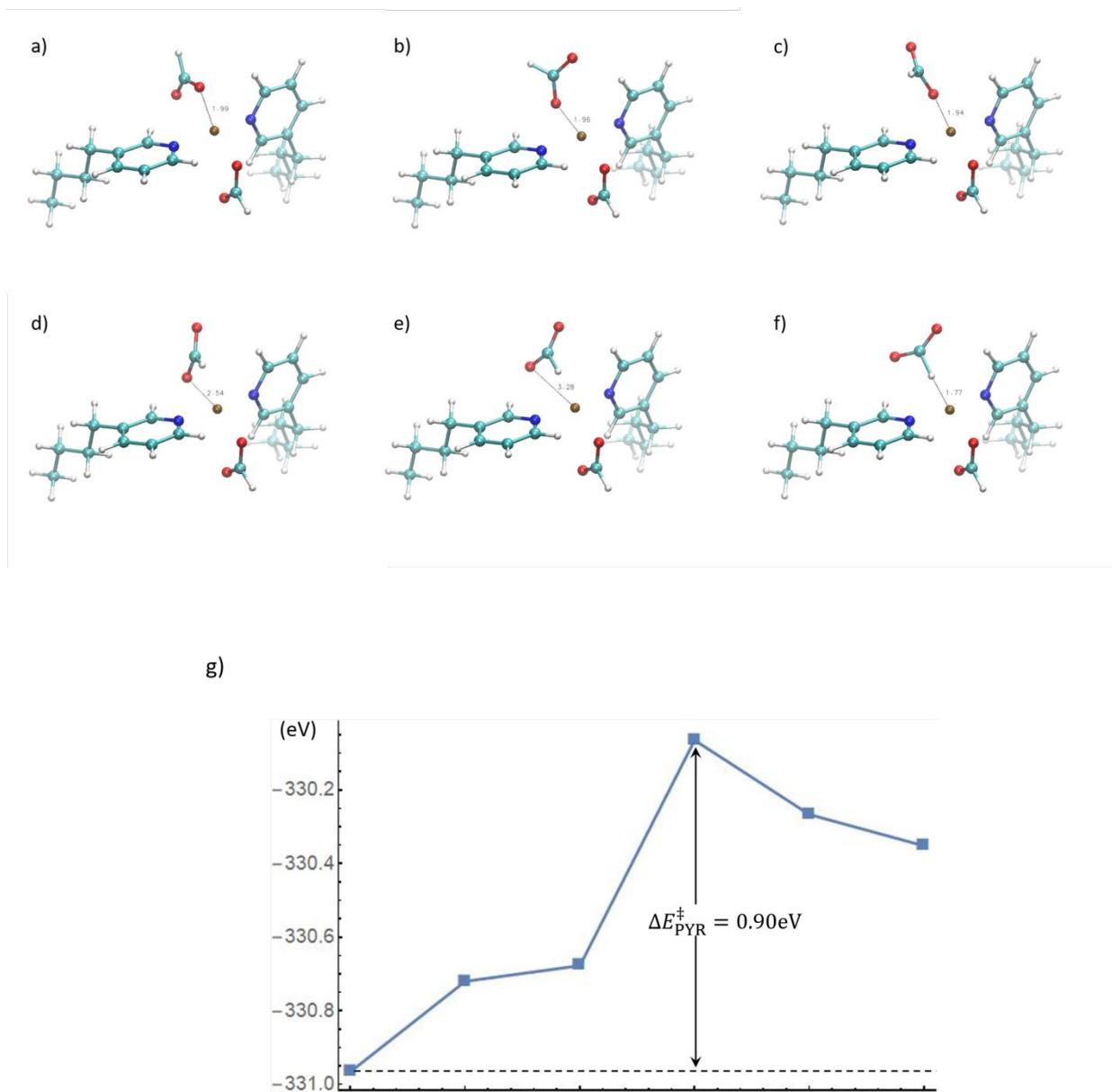
**Scheme S1.** Proposed pathways for intermolecular dihydrogen formation on Cu (II) formate amine compound.



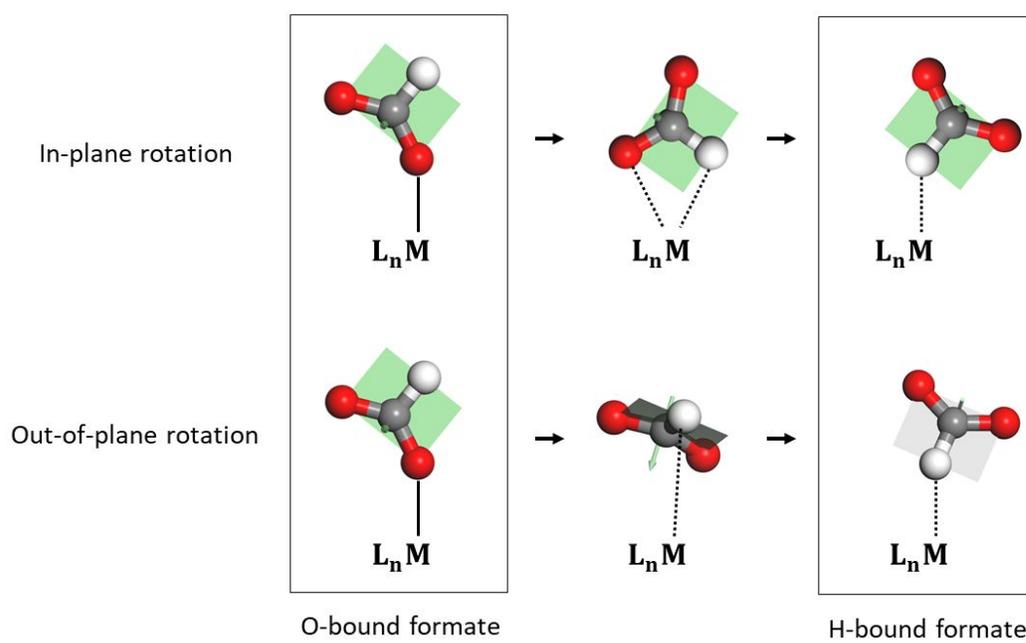
**Figure S1.** FTIR measurement of anhydrous copper formate vs. octylamine-copper-formate complexes: The asymmetric ( $\sim 1600\text{ cm}^{-1}$ ) and symmetric ( $\sim 1350\text{ cm}^{-1}$ ) carbon-oxygen stretching frequencies of the COO bonds of anhydrous copper formate and copper formate coordinated to octylamine. The geometry adopted between the copper center and COO<sup>-</sup> will influence the carboxylate C-O bond lengths and O-C-O angle which in turn affects the wavenumbers of the symmetric ( $\nu_{\text{sym}}$ ) and antisymmetric ( $\nu_{\text{asym}}$ ) stretching frequencies. Low  $\Delta$  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 ( $\Delta$ ) 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  $\Delta$  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.



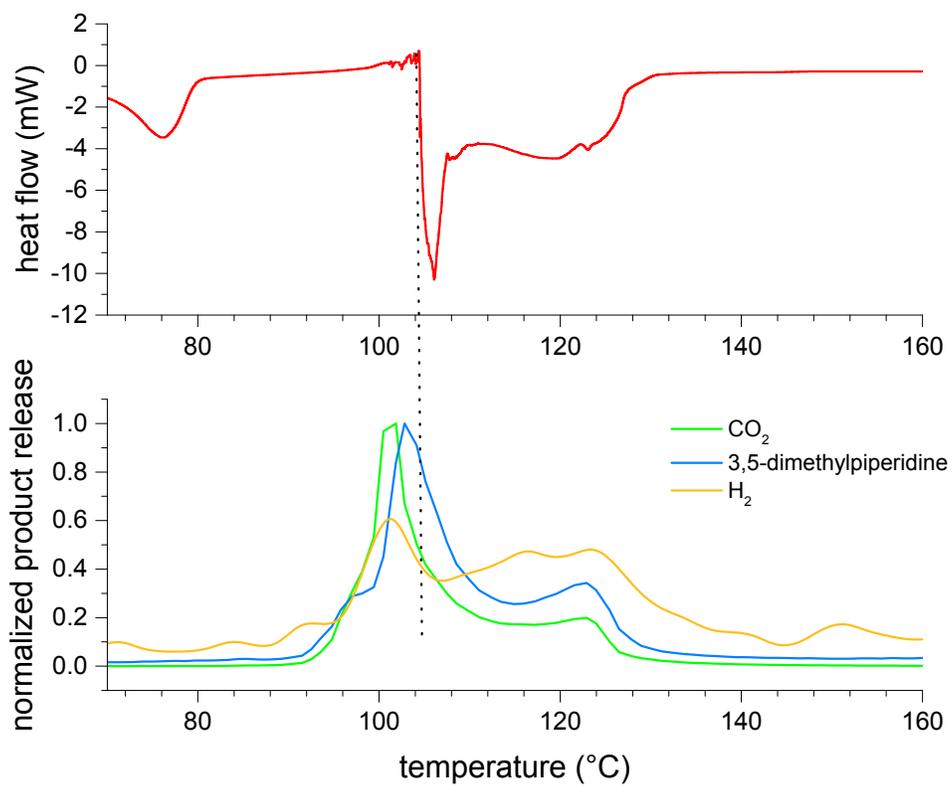
**Figure S3.** Minimum energy configurations and energies upon formate rotation for bis(3-butylpyridine) copper formate: a) the reactant; b)-e) 4 intermediate configurations with d) corresponding to TS; f) the product; g) the energy profile calculated by NEB method.



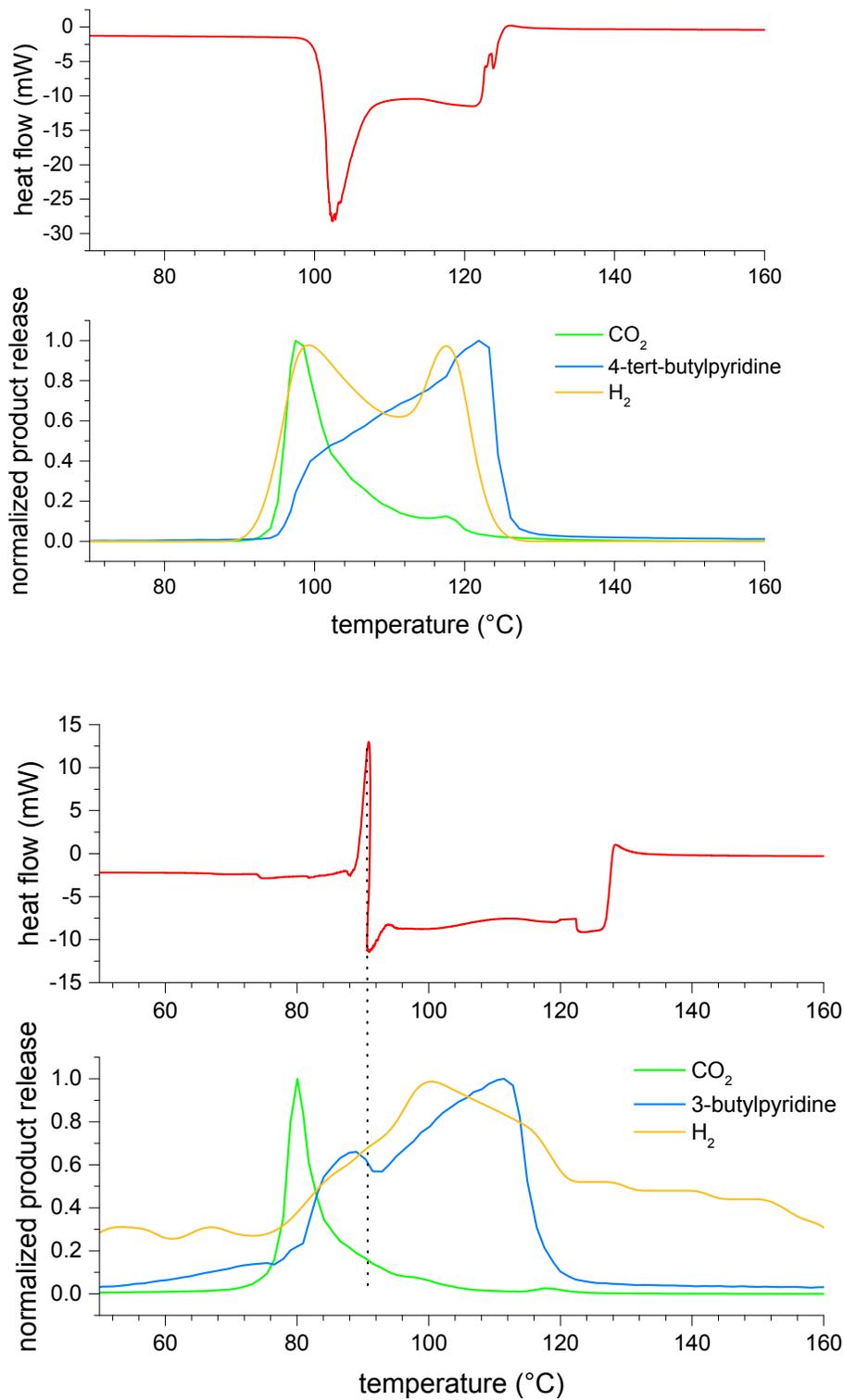
**Figure S4.** A schematic to describe the difference between “out-of-plane” and “in-plane” rotations that transform the O-bound to H-bound formate configuration.

	Dimeric Cu(II)-Cu(II) complexes	Dimeric Cu(I)-Cu(I) complexes after H2 dissociation	Dimeric Cu(I)-Cu(I) complexes after ligands dissociation
Cu-PA			
	$E_t = -210.2 \text{ eV}$	$E_t = -203.6 \text{ eV}$	$E_t = -131.2 \text{ eV}$
Cu-SA			
	$E_t = -275.0 \text{ eV}$	$E_t = -268.4 \text{ eV}$	$E_t = -163.8 \text{ eV}$
Cu-PYR			
	$E_t = -352.0 \text{ eV}$	$E_t = -345.3 \text{ eV}$	$E_t = -202.4 \text{ eV}$

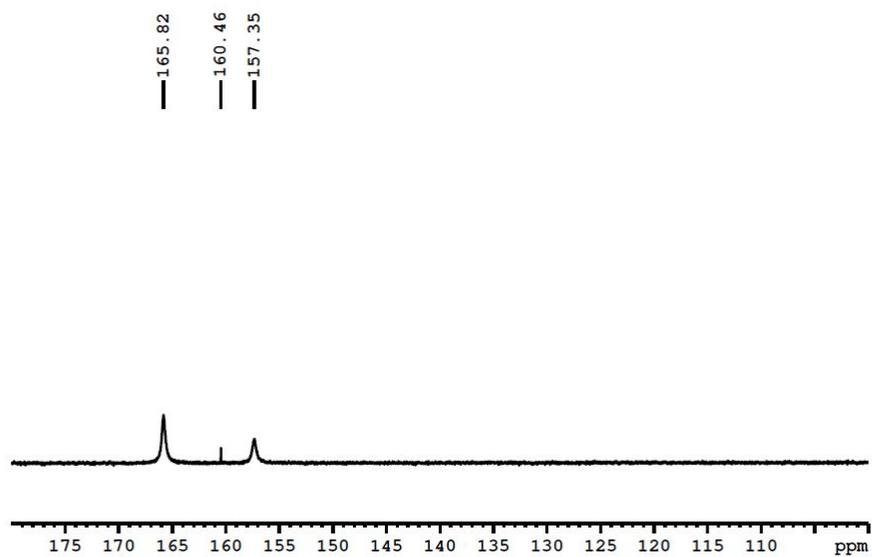
Figure S5. Optimized structures and total energies of dimer compounds.



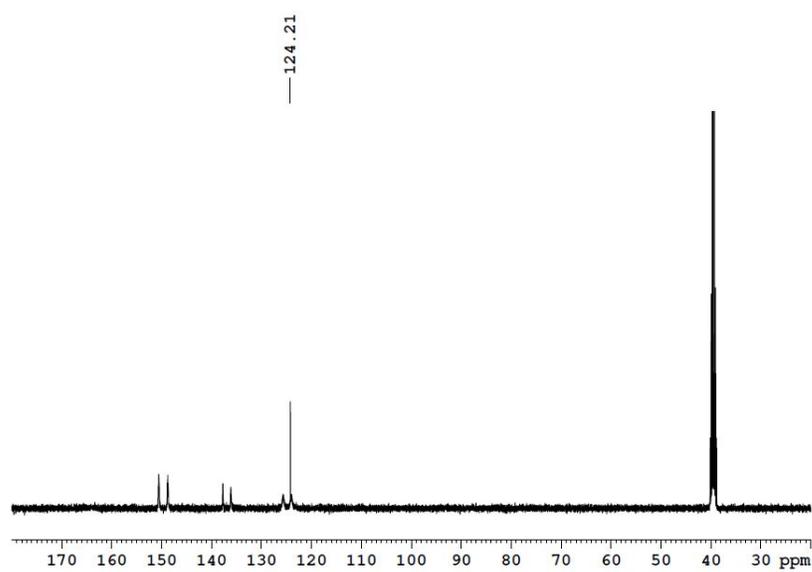
**Figure S6.** DSC-TGA-FTIR –MS curves of the thermolysis of bis(3,5-dimethylpiperidine) copper formate.



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

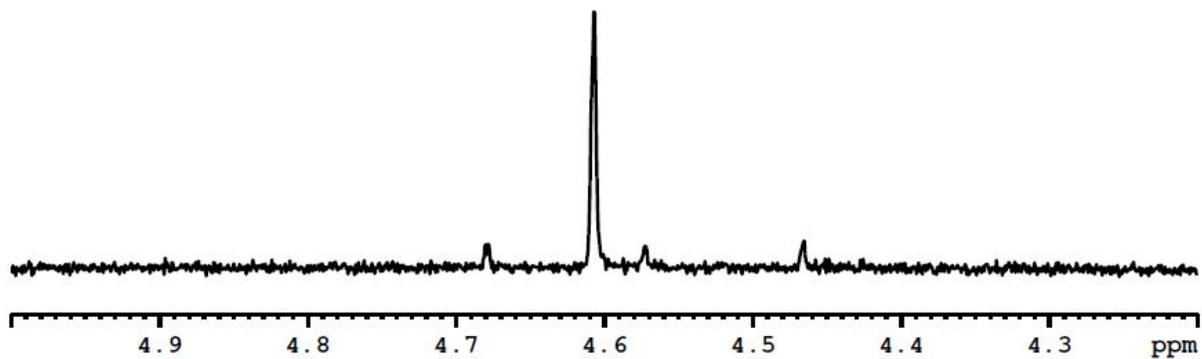


a.

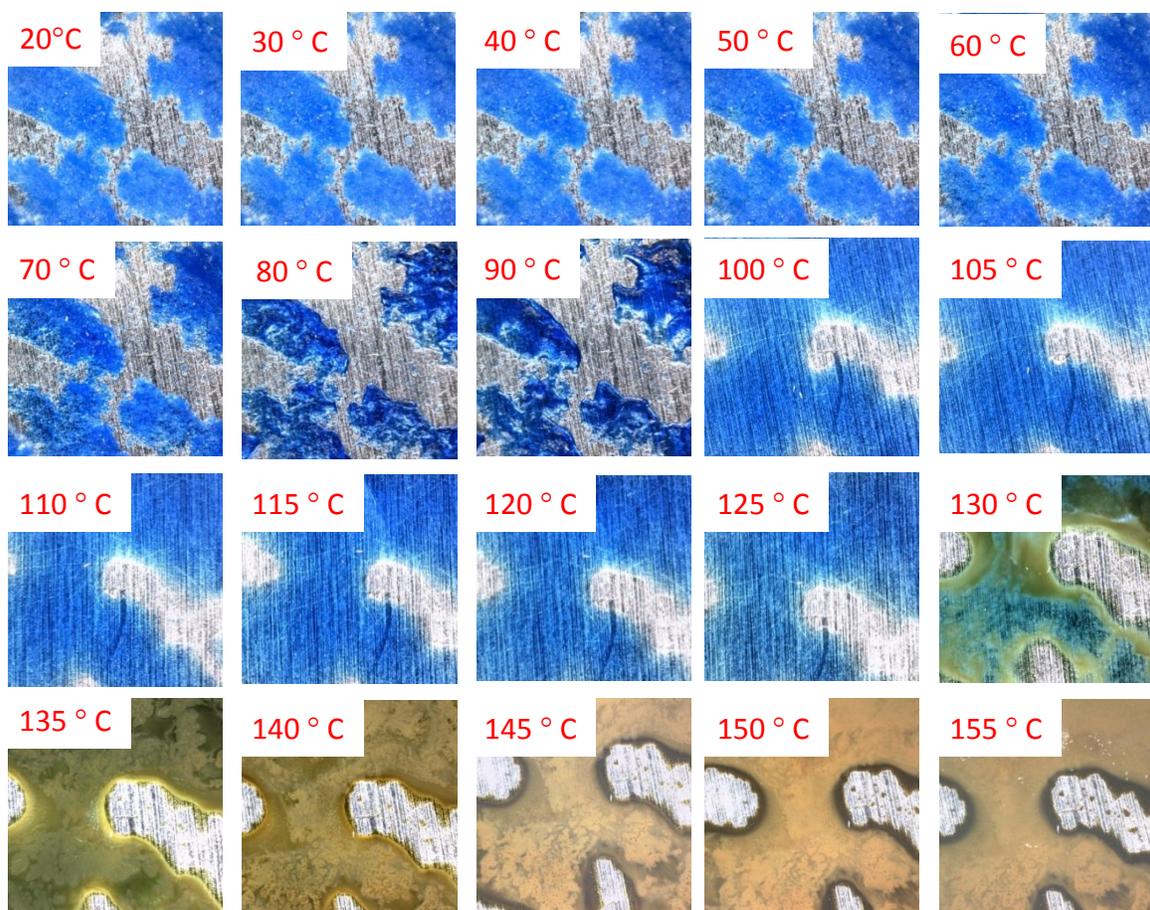


b.

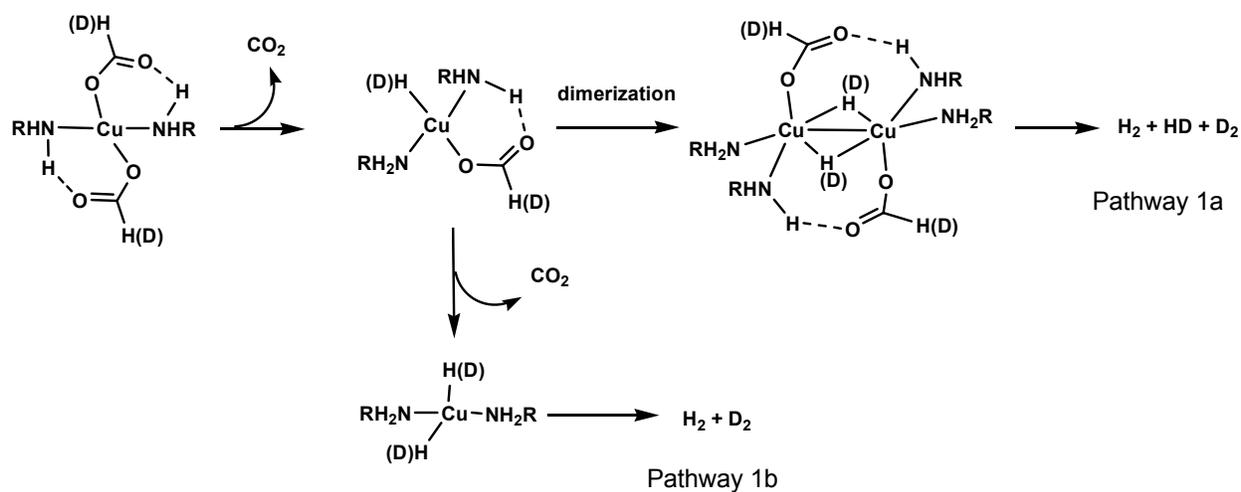
**Figure S8.** a)  $^{13}\text{C}$  NMR of Cu-OCT heated to  $80^\circ\text{C}$  for 1 hour; b)  $^{13}\text{C}$  NMR of Cu-PY heated at  $90^\circ\text{C}$  for 5 minutes.



**Figure S9.**  $^1\text{H}$  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  $90^\circ\text{C}$  for 35min, H<sub>2</sub>:HD around 1:1 (mole ratio).



**Figure S10.** Optical microscopy images of the Cu\_OCT complex at various temperatures. Phase transitions are present near  $\sim 80\text{-}90^\circ\text{C}$  and  $90\text{-}100^\circ\text{C}$ . 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<sub>2</sub>, HD and D<sub>2</sub> 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<sub>2</sub> and D<sub>2</sub> only.