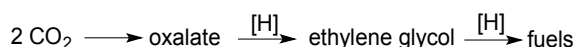


**Principal Investigators:** Professors T. Daniel P. Stack & Christopher E. D. Chidsey

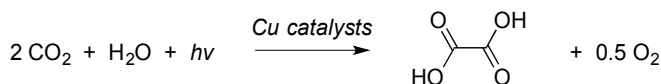
**Project Title:** Reductive Bond Formation with Carbon Dioxide and Water Oxidation: Immobilized Copper Complexes as Discrete Electrocatalysts on Carbon Surfaces.

**1. Project Objectives:** Developing discrete, copper-based electrocatalysts for reductive coupling of CO<sub>2</sub> and water oxidation on carbon-based materials.

**2. Project Summary:** The production of carbon-based fuels and chemicals from both renewable energy and materials is of utmost importance for a sustainable and energy-efficient society. The emerging technologies that directly convert sunlight to energy serve as an important starting point in creating a renewable energy economy, but its intermittent and diffuse availability require that the harvested energy be transformed to high energy density and storable fuels. Developing energy-efficient processes that reductively couple CO<sub>2</sub>, an abundant and renewable C<sub>1</sub> source, for the production of value-added chemicals with electrons derived from water oxidation is a goal of great importance. Currently, less than 1% of anthropomorphic CO<sub>2</sub> is used for the production of chemicals. A game-changing strategy would be the synthesis of higher order C<sub>n</sub> (n > 1) products and fuels from CO<sub>2</sub>, but this practice is limited due to the extreme challenges associated with C-C bond formation and water oxidation under energy-efficient conditions. Developing catalysts capable of efficiently coupling CO<sub>2</sub> to oxalate and subsequently to other C<sub>2</sub> compounds would provide a novel strategy to make value-added chemicals not dependent on fossil fuel reserves.



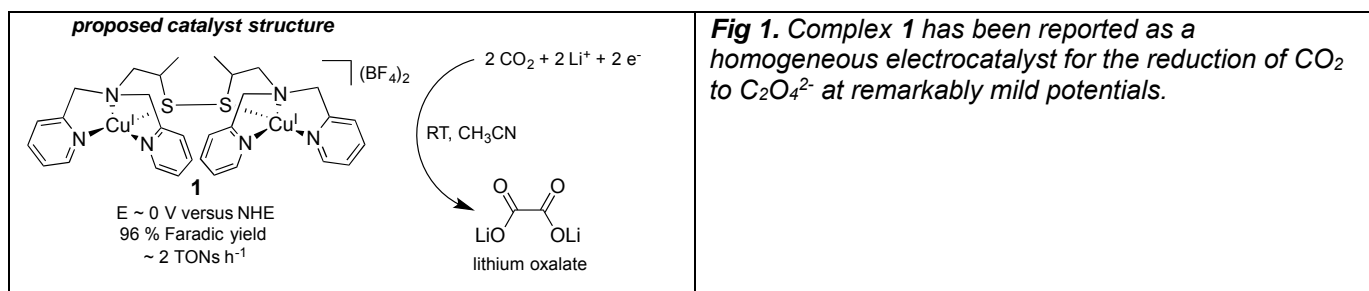
A long-term vision is the capture and conversions of CO<sub>2</sub> from gas- or coal-fire power plants to large-scale, value-added chemicals or fuels with electron derived from solar-powered water oxidation. The overall transformation resembles photosynthesis, in which nature uses solar power to drive the conversion of CO<sub>2</sub> and water to C<sub>n</sub> chemicals and O<sub>2</sub>.



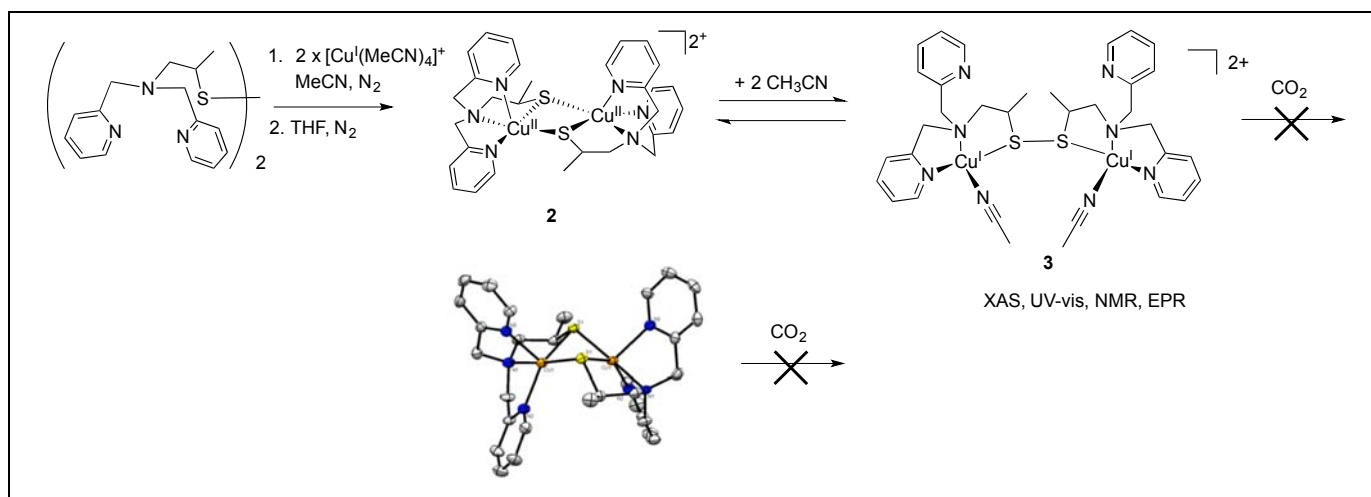
The ongoing research focuses on the development of copper catalysts attached to and specifically positioned on inexpensive carbon electrodes for electrocatalytic CO<sub>2</sub> reduction or water oxidation. The proposed research entails ligand synthesis, homogeneous catalyst screening, catalyst immobilization on carbon surfaces, and mechanistic analyses, along with complementary density functional theory (DFT) calculations.

### 3.1 Homogeneous CO<sub>2</sub> Reduction by Cu(I) Complexes:

We have investigated the reductive coupling of CO<sub>2</sub> to oxalate by simple copper complexes. The addition of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> to the disulfide ligand is reported in the literature to yield a μ-disulfido Cu(I)Cu(I) complex (**1**) capable of stoichiometrically and electrocatalytically coupling CO<sub>2</sub> to oxalate (**Fig 1**) at remarkably mild potentials.<sup>1</sup>

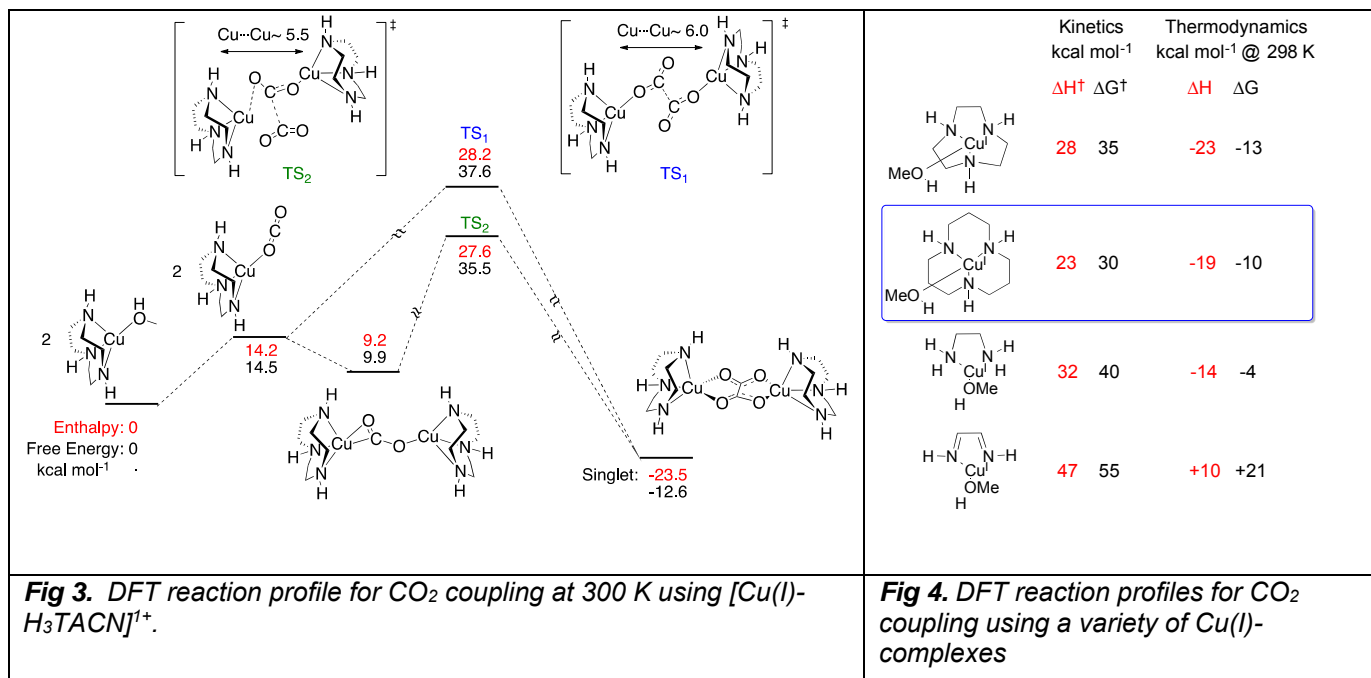


In our hands, the solid state x-ray structure shows that the disulfide bond is reduced upon the copper coordination to give a μ-thiolato Cu(II)Cu(II) dimeric structure (**2**). Spectroscopic evidence (X-ray Absorption Spectroscopy, UV-vis spectroscopy, NMR) suggest that a μ-disulfido Cu(I)Cu(I) species (**3**) is in equilibrium with **2** in an acetonitrile solution (**Fig 2**), yet we have found no evidence of stoichiometric or electrocatalytic CO<sub>2</sub> reductive coupling to oxalate with this complex.<sup>1</sup> A paper detailing redox behavior of the ligand has been published.<sup>2</sup>



**Fig 2.** Data show the formation of a Cu<sup>II</sup>-thiolate (**2** with its x-ray structure). Cu<sup>I</sup>-disulfide species **3** resemble closely the Cu<sup>I</sup>-disulfide species **1** proposed by Bouwman et al. <sup>1</sup>

DFT calculations suggest that the coupling free energy barriers of CO<sub>2</sub> to oxalate with Cu(I)-aza macrocyclic complexes are reasonable, as low as 30 kcal mol<sup>-1</sup> (**Fig 4**). Such barriers would lead to very slow reaction rates under ambient conditions, but higher temperatures might be viable (**Fig 3 & 4**). The potential energy surfaces of an entire family of Cu(I)-aza macrocyclic complexes were calculated to determine the lowest coupling barrier. In each case, an asymmetric transition state is correlated with the lowest free energy barrier. In all cases, the reaction is calculated to be exergonic. With this information, we screened a variety of Cu(I) aza-macrocycles for CO<sub>2</sub> coupling both at ambient and elevated temperature, but under no conditions could we detect oxalate formation.

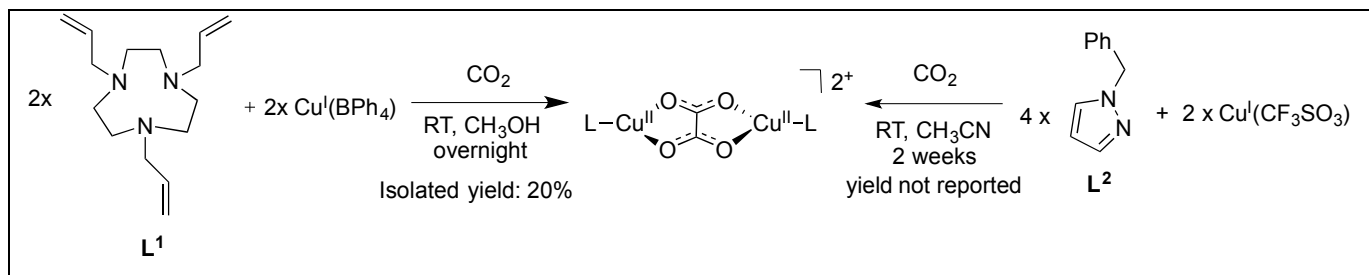


**Fig 3.** DFT reaction profile for CO<sub>2</sub> coupling at 300 K using [Cu(I)-H<sub>3</sub>TACN]<sup>1+</sup>.

**Fig 4.** DFT reaction profiles for CO<sub>2</sub> coupling using a variety of Cu(I)-complexes

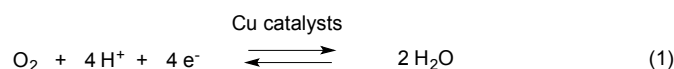
Two other Cu complexes with nitrogen-based ligands are reported in the literature to promote stoichiometric formation of oxalate products under remarkably mild conditions (**Fig 5**).<sup>3,4</sup> By literature precedent, the CO<sub>2</sub> reaction with the Cu(I) complex formed with the more electron-donating triazacyclononane (TACN) ligand (**L**<sub>1</sub>) is

faster than that with the aromatic nitrogen ligand (**L**<sub>2</sub>), but in both cases the oxalate yield is low and characterization has relied solely on x-ray crystallography. As above, we have explored the coupling capacity of these two complexes with CO<sub>2</sub>,<sup>3</sup> and do not find any significant oxalate formation under a condition attempted. We must conclude from our investigations that coupling of CO<sub>2</sub> using cationic azamacrocyclic Cu(I) complexes is not a viable strategy to oxalate formation at temperatures below 100°C.

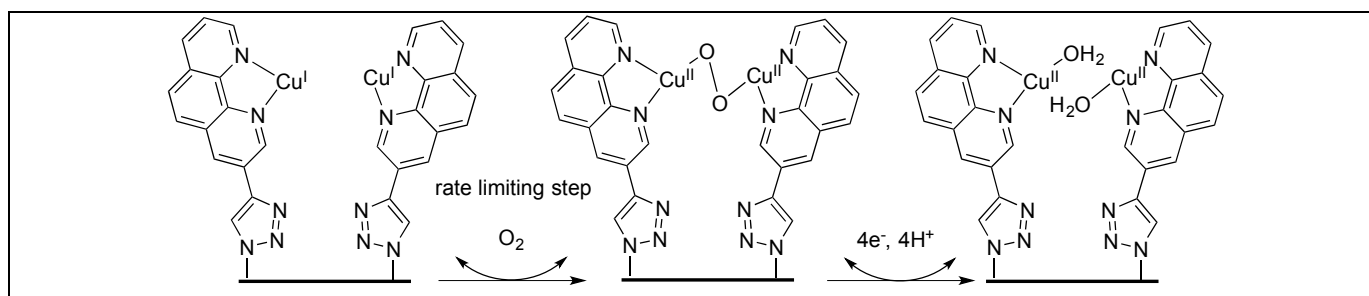


**Fig 5.** Literature examples of Cu<sup>I</sup>-mediated reductive coupling of CO<sub>2</sub> to oxalate.<sup>3,4</sup>

### 3.2 Immobilized Discrete Copper Electrocatalysts for O<sub>2</sub> Reduction:

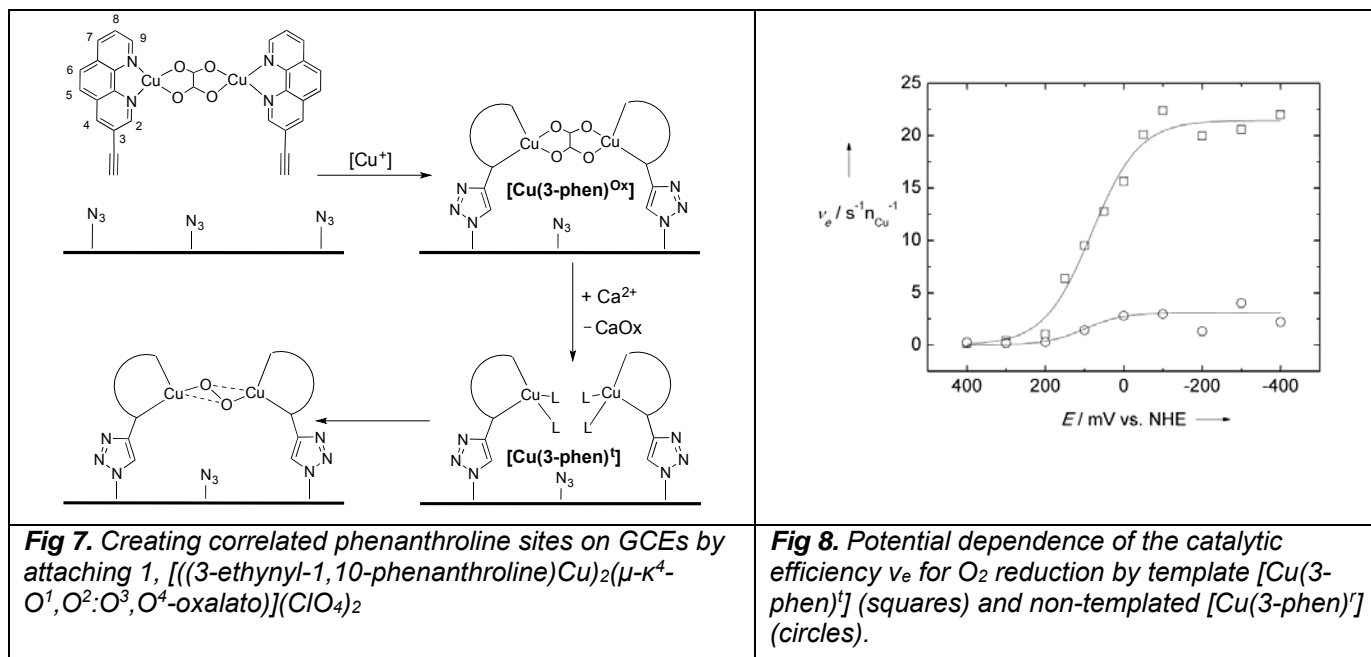


Water oxidation and dioxygen reduction are microscopic reverse processes (eqn 1) that share common reaction mechanisms. The ability of discrete copper complexes to catalyze the electro-oxidation/reduction of water/dioxygen is well documented.<sup>5-7</sup> Studies of dioxygen reduction will inform on how to design electrocatalysts for efficient water oxidation. Using a methodology developed in our labs, Cu(1,10-phenanthroline) complexes have been attached covalently to glassy carbon electrodes (GCE). The ability to reduce O<sub>2</sub> efficiently is related to the number of dinuclear copper sites on the electrode.<sup>5</sup> Meyer *et al.* have demonstrated recently that the electrocatalytic rate of water oxidation by copper catalysts have a second-order rate dependence on the copper catalyst.<sup>7</sup> Although our previous work has focused on O<sub>2</sub> reduction, the principles for creating dinuclear species should be applicable to water oxidation (**Fig 6**).



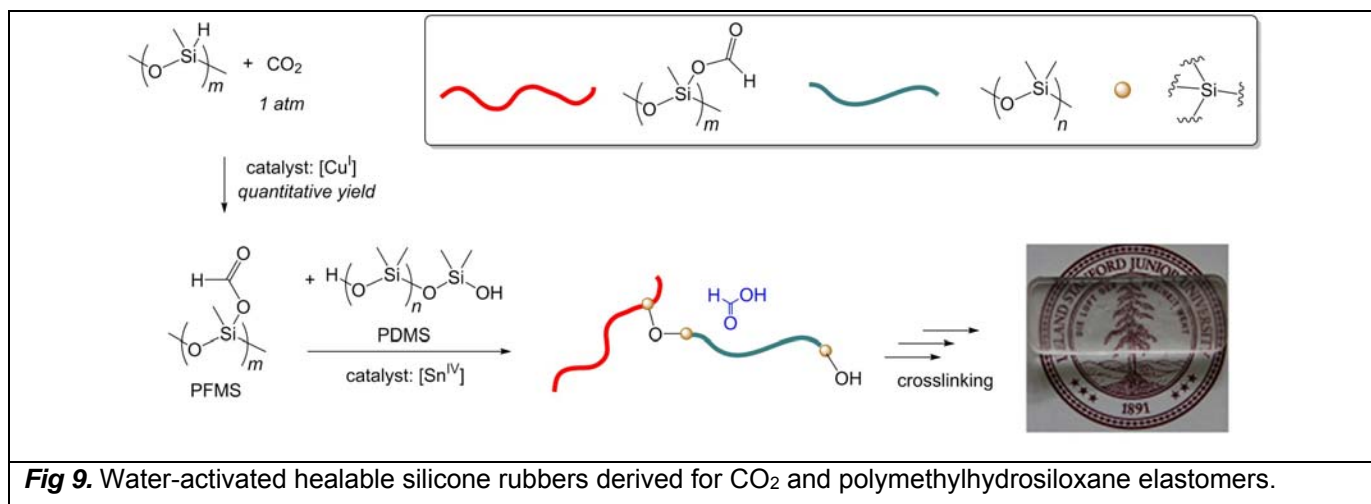
**Fig 6.** Schematic illustrations of dioxygen reduction and water oxidation, two microscopically reversible processes, catalyzed immobilized dinuclear copper complexes

The catalysts are immobilized through a 1,3-dipolar azide-alkyne cycloaddition between a ligand with an ethynyl group and an azide moiety on the GCE surface.<sup>8</sup> Polynuclear ligand binding sites can be created effectively on a GCE by two methods: (a) controlled azide surface density or (b) templating dinuclear sites by immobilization of complexes with a removable bridge, an imprinting technique. The oxalate anion has been used successfully to imprint dinuclear Cu phenanthroline sites (**Fig 7**), even under surface-diluted conditions. A comparison of the kinetic current from O<sub>2</sub> reduction versus copper catalyst surface coverage of both randomly distributed Cu-phenanthroline complexes and imprinted dimeric sites shows significantly more current (~10-fold increase) with the latter exhibiting a greater faradaic efficiency to water (**Fig 8**), highlighting the importance of a correlated arrangement of the metal centers on the electrode surface for fast and energy efficient conversions.



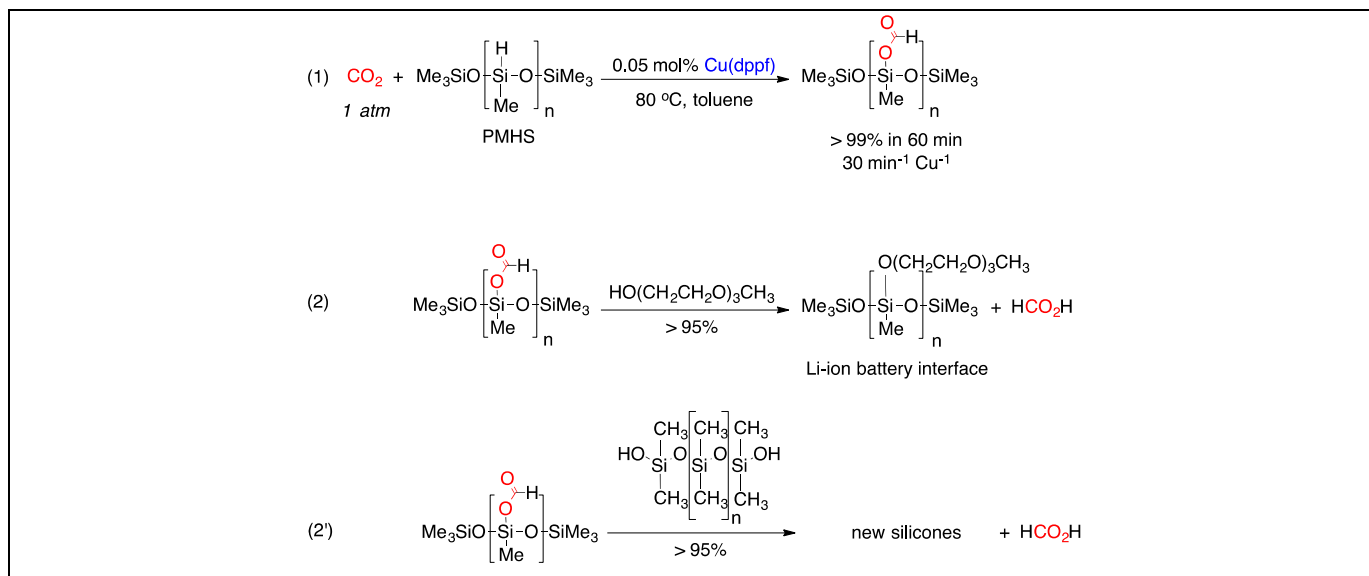
### 3.3 Hydrosilylation of $\text{CO}_2$ – Reductive Coupling to Formic Acid and New Silicone Materials

In the process of investigating  $\text{CO}_2$  coupling with discrete copper complexes, we have discovered a facile, quantitative hydrosilylation of  $\text{CO}_2$  by polyhydrosiloxane to prepare formoxylated polysiloxane. The resulting formoxylated polysiloxane releases formic acid when treated with water or an alcohol, completing the  $\text{CO}_2$  to fuel objective, but more importantly, this material crosslinks readily to an elastomeric silicone that exhibits thermal healable behavior even in the presence of water. A highly efficient  $\text{Cu}(\text{I})$  hydride catalyst is a key enabling step to these new smart materials from two by-products, polyhydrosiloxane and  $\text{CO}_2$ . A paper detailing this investigation is under review <sup>10</sup>.



This paper details a new strategy for the reductive integration of  $\text{CO}_2$  into a polymeric elastomer with healing properties that is tolerant of wet conditions. Efficient  $\text{CO}_2$  hydrosilylation using an earth-abundant metal catalyst allows for the simple formation of formoxylated polysiloxane (PFMS) from two abundant industrial by-products in 1 hour. Engineering of latent reactive groups that generate healing components *in situ* upon damages provides a new approach for future polymer-healing designs. Further explorations of PFMS as a crosslinking component in silicone rubbers may provide greener alternatives to commercial acetoxy silanes, in which the carbons are derived exclusively from fossil fuels. The remarkably high mass ratio of  $\text{CO}_2$  in the formoxylated polysiloxane (ca.

40%) and in the formed elastomers (ca. 4-10%) unequivocally demonstrates the great potential of CO<sub>2</sub> as a useful carbon source to make polymers via a reductive approach. However, compared to the sheer scale biosynthesis of lignocellulose biomass, more research efforts to develop new CO<sub>2</sub> polymerization strategies are needed.



**Fig 10.** Water-activated healable silicone rubbers derived for CO<sub>2</sub> and polymethylhydrosiloxane elastomers.

### 3.4 Development of Robust and Reproducible Attachment Points to High-Surface Area Carbons

Developing efficient and reproducible covalent surface functionalization methods for high surface area, porous carbon materials is an area of considerable research interest due to their low cost. Surface modification allows for tuning the chemical and physical properties of these materials increasing the range of their applications, including energy storage and gas separations. Ideally, introduced functionality is robust and provides a versatile attachment point for further chemical modification. Current carbon surface functionalization strategies such as radical coupling of amines, coupling of alkynes at high temperatures, and photochemical coupling of alkynes are limited in scope, relatively unselective, and often require aggressive reaction conditions.

Chloromethylation of high-surface carbons is possible with good coverage of ca. 1.5 mmol g<sup>-1</sup>, yet the hazardous procedure is difficult to perform and yields an electrophile for nucleophilic displacement that is far from ideal if high derivatization yields are desired.<sup>11</sup> We have developed and optimized simple, safe and reproducible bromomethylation of high-surface area carbons. The bromomethylated materials (**Br-AC**) have high surface coverage (ca. 1.2 mmol g<sup>-1</sup>), exhibit excellent stability (100 days, < 5 % Br loss), and readily react with a variety of nucleophiles in high yields. Derivatization with azide is a particularly attractive material (**N<sub>3</sub>-AC**) for further derivatization using Cu(I) catalyzed azide-alkyne cycloaddition reaction (CuAAC). **N<sub>3</sub>-AC** also display excellent stability and can be coupled with various terminal alkynes to yield functional materials, as detailed below.

Treatment of **Br-AC** with sodium azide in DMSO affords **N<sub>3</sub>-AC** with typically greater than 90 % conversion of Br to N<sub>3</sub>, as determined by nitrogen elemental analysis (EA), and in agreement with XRF data for **N<sub>3</sub>-AC** showing only 4 – 8 % of the initial Br content remaining after the reaction. The Br 3d and N 1s regions of the XPS spectrum of **N<sub>3</sub>-AC** confirm the high conversion of Br to N<sub>3</sub>.

In addition to functionalization of **Br-AC** by simple nucleophilic displacement, CuAAC has been performed on **N<sub>3</sub>-AC** with various terminally alkynylated substrates. Ethynyl ferrocene was first chosen as a model substrate to provide an elemental tag (Fe) for characterization by XRF and XPS. CuAAC of ethynyl ferrocene on **N<sub>3</sub>-AC** resulted in ferrocene-functionalized materials (**Fc-AC**) with Fe loadings of up to 1.0 mmol g<sup>-1</sup> as measured by XRF, corresponding to approximately 90% conversion of azide from **N<sub>3</sub>-AC**. The N 1s region of the XPS spectrum of **Fc-AC** displays a single peak near 401 eV, suggesting good conversion of azide to triazole during the CuAAC reaction. The Fe 2p<sub>3/2</sub> region shows distinct features associated with Fe(II), confirming incorporation of Fe onto the surface of AC.<sup>12</sup>

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