Final Report

The Direct Ocean Electrocapture (DOE) project aims to develop novel bicarbonate-absorbing materials—especially metal–organic frameworks (MOFs)—for energy-efficient CO_2 capture from seawater. In our Interim Report, we identified aminoguanidines as a promising starting point because they can be redox-active and have a documented strong affinity for bicarbonate (Figure 1). We therefore began by synthesizing a model compound to evaluate both (i) redox behavior and (ii) bicarbonate uptake.

As is often the case in early-stage chemistry, our first design was not ultimately suitable, so we ran several rounds of a design → test → redesign cycle. The good news is that this process led us to a new direction: we discovered a novel class of aminoguanidine-based polymers that can be made straightforwardly from commercially available building blocks and appear to offer multiple promising paths for further development. Below we summarize the journey and key findings.

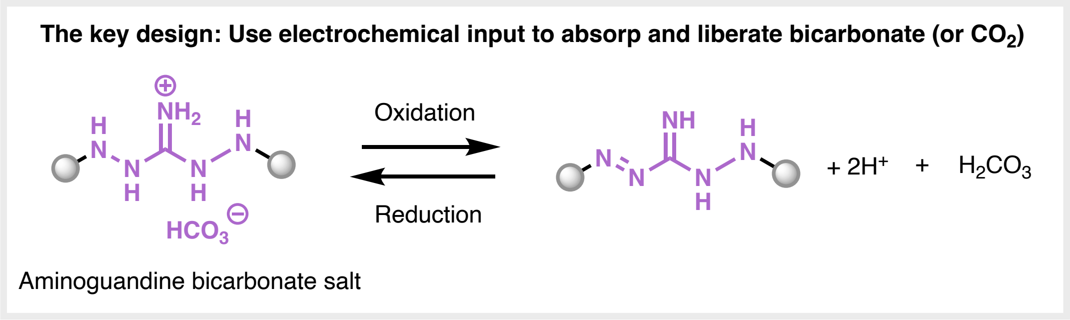
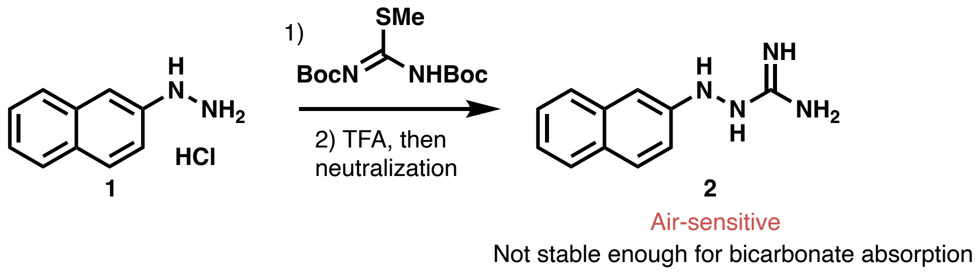


Figure 1. The key mechanism for redox-based reversible bicarbonate capture

Summary of the study

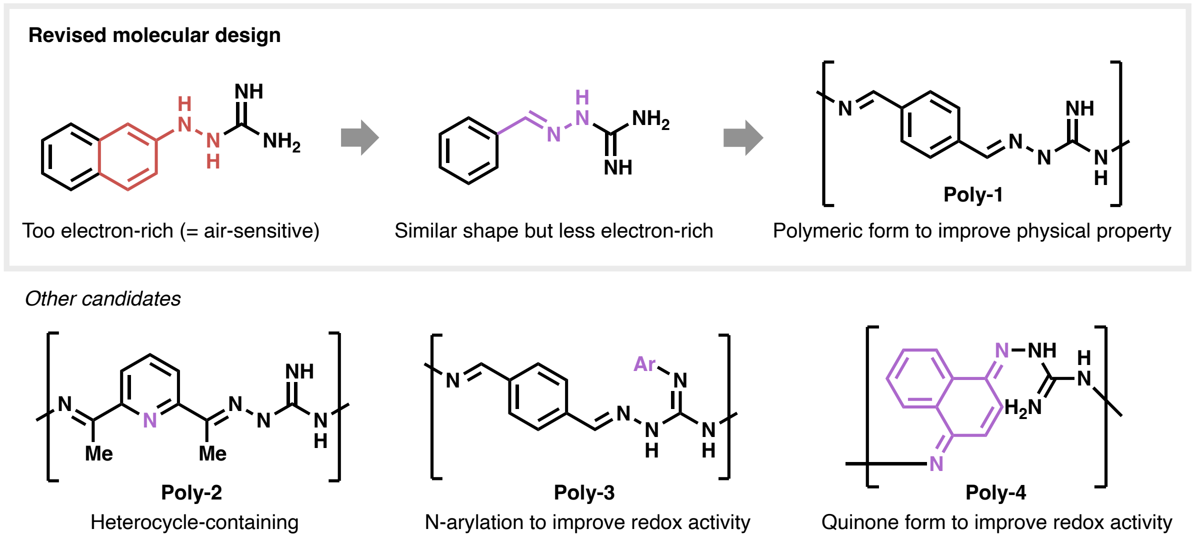
Our first model compound was 2-naphthylaminoguanidine **2** (Figure 2), prepared by guanidylation of 2-naphthyl hydrazine **1**. We quickly found that compound **2** is air-sensitive, consistent with its highly electron-rich structure. Cyclic voltammetry showed an oxidation onset around 0 V (vs Ag/AgCl), supporting the observation that it readily oxidizes under ambient aerobic conditions. While air sensitivity may not be a fundamental problem for the eventual application (the material will cycle between oxidized and reduced states during operation), it makes laboratory characterization difficult because the sample composition changes during routine handling.



Air-sensitive
Not stable enough for bicarbonate absorption

Figure 2. Synthesis of 2-naphthylaminoguanidine

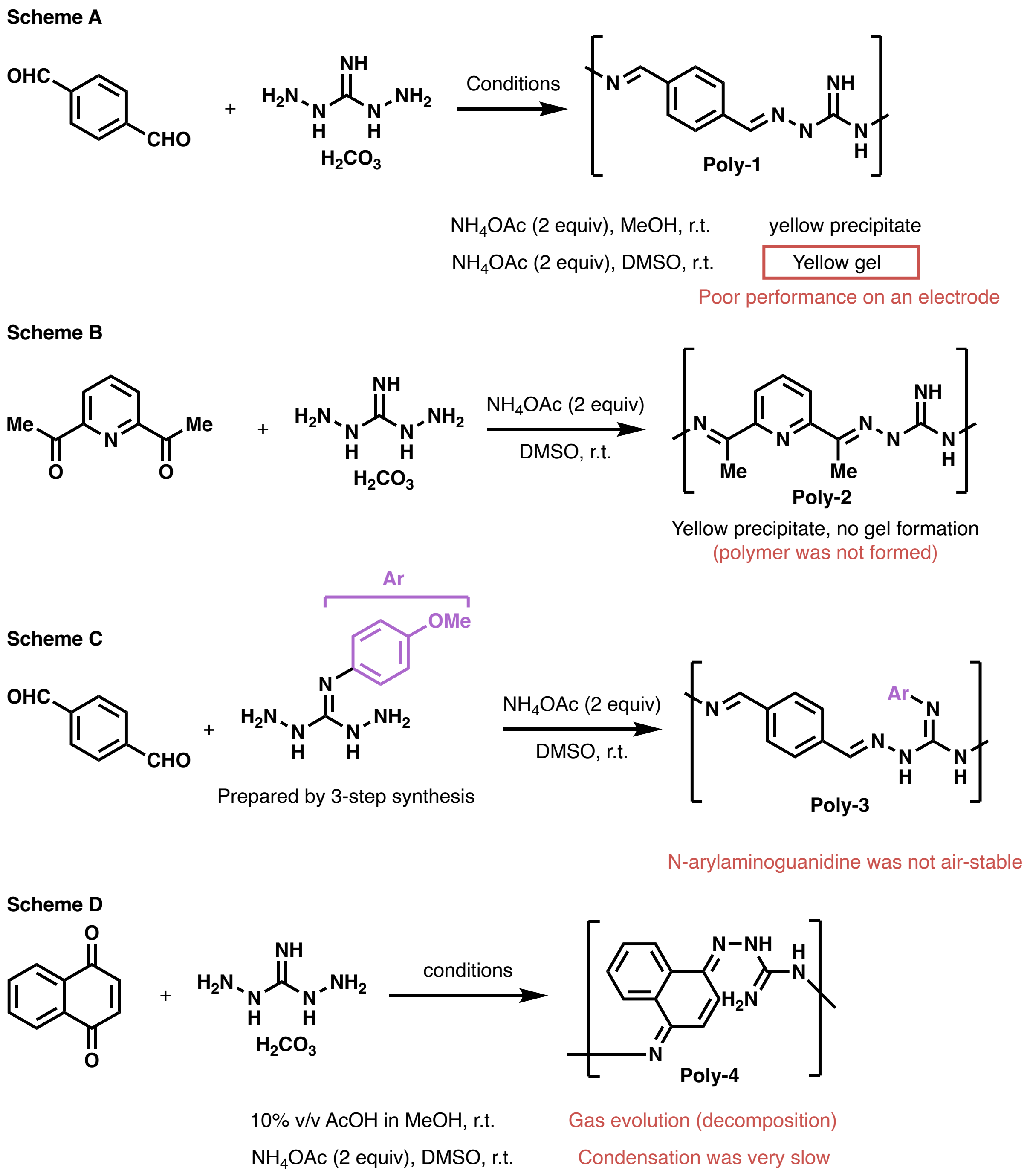
To address this, we revised the molecular design to improve air stability (Figure 3). We believe the sensitivity of **2** primarily arises from the Ar–NH–NH linkage, where the naphthalene π-system and adjacent nitrogen lone pairs create excessive electron density. To reduce electron density with minimal structural disruption, we incorporated a C=N unit. Because the practical target material needs to be a solid-state, polymeric system (either a polymer itself or integrated into a MOF-like framework) was considered more suitable, and **Poly-1** was designed as the polymeric counterpart of this revised motif, along with related candidates **Poly-2** to **Poly-4**.



Too electron-rich (= air-sensitive)
Similar shape but less electron-rich
Polymeric form to improve physical property
Heterocycle-containing
N-arylation to improve redox activity
Quinone form to improve redox activity

Figure 3. Revised molecular design

The preparation of **Poly-1** to **Poly-4** is outlined in Schemes 1–4. In general, the syntheses involve a straightforward condensation between a commercially available dialdehyde and N,N′-diaminoguanidine. We screened multiple condensation conditions (solvent and additives to tune pH) to form polymeric materials. For **Poly-1**, a bright yellow gel was formed using DMSO as solvent with ammonium acetate as an additive. Encouraged by this successful polymer formation, we transferred the material onto an electrode to study its electrochemical behavior. Unfortunately, upon drying the polymer became a brittle solid and peeled off the electrode, preventing further electrochemical testing in that format. For **Poly-2** to **Poly-4**, similar condensation conditions were explored, but polymer formation was inefficient and/or the resulting materials were not stable.



Scheme A:
NH$_4$OAc (2 equiv), MeOH, r.t. — yellow precipitate
NH$_4$OAc (2 equiv), DMSO, r.t. — Yellow gel
Poor performance on an electrode

Scheme B:
Yellow precipitate, no gel formation
(polymer was not formed)

Scheme C:
Prepared by 3-step synthesis
N-arylaminoguanidine was not air-stable

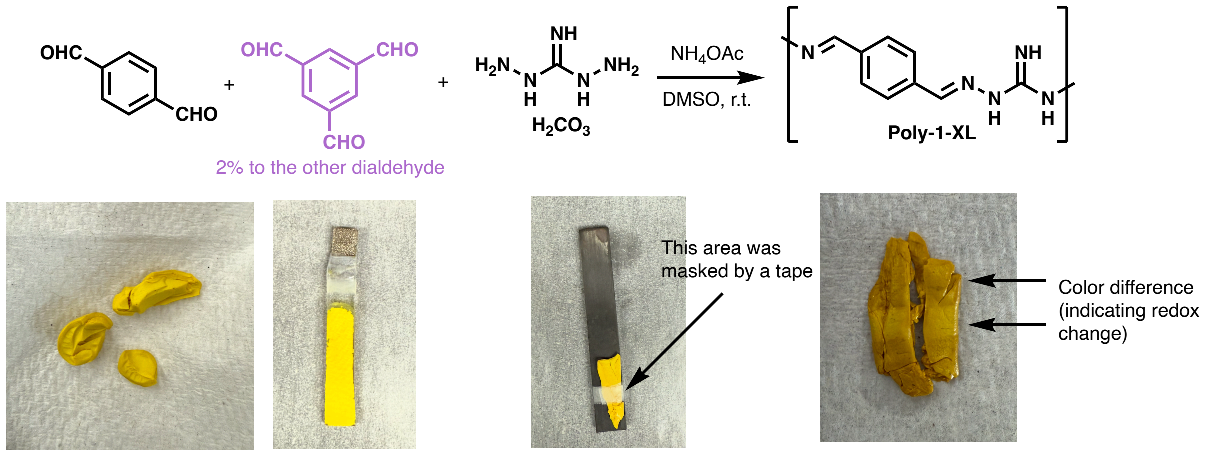
Scheme D:
10% v/v AcOH in MeOH, r.t. — Gas evolution (decomposition)
NH$_4$OAc (2 equiv), DMSO, r.t. — Condensation was very slow

Figure 4. Syntheses of ***Poly 1-4***

After evaluating additional polymer designs, we concluded that **Poly-1** was the most worthwhile candidate to pursue further due to accessibility and facile polymerization. It forms reliably and reproducibly; the major barrier appears to be physical handling/film robustness, rather than fundamental chemistry. In addition, to the best of our knowledge, aminoguanidine-based condensation polymers of this type have not been previously reported, which increases the potential value of this discovery.

To address the mechanical fragility, we pursued cross-linking—a standard strategy to improve polymer robustness by increasing connectivity between polymer chains. Specifically, we introduced a small amount of a trialdehyde cross-linker (2–5% relative to the dialdehyde) during polymerization to form **Poly-1-XL** (Figure 5). Gratifyingly, this approach was highly effective: the resulting material is soft and rubbery, an ideal mechanical profile for processing and handling.

Next, to evaluate electrochemical behavior in a practical format, the polymer precursors were mixed and immediately cast onto an ITO (conductive glass) electrode, where the film was cured. The resulting coating adhered well, enabling preparation of a robust polymer-coated electrode for testing. When the electrode was connected to an electrolysis cell and polarized, the polymer layer largely insulated the underlying ITO, indicating that the material is not intrinsically electronically conductive. This outcome is not surprising: many redox-active polymers require ionic dopants and/or conductive additives (e.g., carbon) to achieve efficient charge transport in the solid state. Importantly, when electrolysis was performed in an alternative configuration—by pressing a bulk polymer sheet against a graphite electrode and masking a part of the polymer with tape—a clear color change was observed in the exposed region relative to the masked area. This visible response strongly suggests that Poly-1-XL undergoes redox switching as intended, but that suitable additives or formulation changes will be needed to translate redox activity into efficient electrochemical performance.



Bulk solid of **poly-1-XL** (left) and casting on ITO electrode (right)

Poly-1-XL on graphite electrode (before electrolysis, left) and appearance after electrolysis (right).

Figure 5. Synthesis of poly-1-XL and its electrochemical behavior.

Conclusion and future path forward

Although our initial plan focused on MOF development, this project unexpectedly opened an exciting and highly promising alternative path: a new class of redox-active aminoguanidine polymers that is straightforward to synthesize from commercially available building blocks. This pivot does not represent a detour from the original goal—rather, it expands the platform. Redox-active polymers share key features with MOFs (solid-state redox cycling and molecular-level tunability), so the design principles and lessons learned here can translate directly into future development for MOF-based bicarbonate capture materials.

Importantly, this polymer platform has substantial standalone value. To the best of our knowledge, these aminoguanidine-based polymers are previously undocumented, and the materials exhibit clear signatures consistent with redox activity. The next priority is therefore not discovery of the chemistry per se, but materials engineering: incorporating additives or secondary phases that improve electronic and ionic transport (e.g., ionic dopants, conductive fillers, or composite architectures) to fully translate intrinsic redox activity into measurable electrochemical performance.

More broadly, the potential impact of this platform extends well beyond bicarbonate absorption. Guanidine motifs are “privileged” ligands for metal binding, suggesting an immediate opportunity for reporposing the same design logic toward metal capture (e.g., removal of toxic metals from waste streams or selective recovery of valuable metals). From a different angle, if the redox capacity proves substantial and cycling is stable, these materials could also serve as battery components (e.g., binders, coatings, or composite phases). Collectively, these results establish a promising foundation for multiple next-generation material applications.

Finally, this project delivered a high return on investment. With a net research budget of $27k (with the remaining $23k covering institutional overhead), we advanced from concept to the discovery and initial validation of a genuinely new class of material—an outcome that typically requires substantially greater resources in today’s research environment. This cost-efficient progress positions the project well for the next stage of development, including follow-on funding and potential industry collaborations.