

Co-catalyst and metal free CO₂ fixation into cyclic carbonates: covalent organic polymers are everything you need

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The non-redox fixation of CO₂ in cyclic and polymeric carbonates is regarded as one of the most promising technologies for small scale CO₂ utilization. Yet, most heterogeneous catalysts reported to date require the use of co-catalysts, harsh reaction conditions and the use of non-base metals. In this issue of Chem, Yavuz and coworkers report the one step synthesis of a new covalent organic polymer that circumvents these issues.

Over the next decades, we, human beings, will face one of the most important challenges we have ever faced: to find a way of maintaining our standards of living with an ever-increasing population without making our planet inhabitable. The rising atmospheric concentration of CO₂, a direct consequence of industrialization and rising living standards, is reaching levels that will soon have extraordinary consequences for our planet. Indeed, despite the implementation of nonemitting energy generation technologies, 35 Gtons of CO₂ are emitted into the atmosphere every year,^[1, 2] which means that, unless radical changes in policy and breakthroughs in technology occur over the next few decades, we will most likely enter the feared 2 degree scenario that the Paris agreement tried to avoid.¹

As William McDonough wisely pointed out 3 years ago, there is still a great misconception about carbon and its unique association with atmospheric CO₂ concentrations: “carbon — the element — is not the enemy. Climate change is the result of breakdowns in the carbon cycle caused by us: it is a design failure. Anthropogenic greenhouse gases in the atmosphere make airborne carbon a material in the wrong place, at the wrong dose and for the wrong duration. It is we who have made carbon toxic [...] In the right place, carbon is a resource and a tool”.² In this line, understanding CO₂ emissions as a design failure of our current energy system is the first step to fix this issue. More importantly, understanding and accepting that carbon, the element, is essential to our lives (we are made of carbon) and to our society (the 20th century is known as the century of polymers because of the extreme impact that these carbon made materials had on our society) may help realize the great opportunity that carbon dioxide utilization offers.³

Once the challenge and opportunities are well understood, one will realize that we should not talk about one single design failure, but about many. We emit anthropogenic carbon dioxide in diverse ways, from huge energy generation stations based on coal, oil derivatives or natural gas to smaller emissions (per emitting unit) in transportation or flaring. Obviously, because of the diverse nature and geographic location of each one of these emissions, thinking of a one single solution to mitigate them would be overly simplistic. For instance, while capture and storage or utilization can be realized at large emitting points with an available network for sequestration or utilization, sequestering other important emissions such as those derived from remote flaring would imply a great energy input in transportation of the captured CO₂.⁴ It is specially for these remote emissions where technological

breakthroughs like the one reported by the team of Yavuz in this issue of Chem⁵ may find an important application niche.

When considering remote emissions, the direct capture of CO₂ in high density form (be it a liquid or a solid) would be preferred. Moreover, the use of additional reductants such as hydrogen and/or harsh reaction conditions, either in terms of temperature or pressure, should be avoided. Ideally, the potential product(s), in addition to containing a high density of CO₂, should have a considerably added value. The catalyst should be solid, reusable and preferably made of abundant elements. The use of co-catalysts or other stoichiometric reactants should be prevented. Last but not least, CO₂ separation and purification steps would add to the overall CO₂ footprint of the capture process and are therefore not desired.

Given these constraints, the non-redox fixation of CO₂ in cyclic and polymeric carbonates through reaction with epoxides is one of the most promising technologies for small scale CO₂ valorization/capture. This traditionally homogeneously catalyzed reaction was first reported in 1969⁶ and offers an attractive route, with a 100% atom efficiency of CO₂, for the production of fine chemicals and polymers. Since then, the scientific community has explored a large number of catalysts and different epoxide substrates. Despite notable achievements, most heterogeneous catalysts reported to date still require the use of co-catalysts, are only active at high temperatures and pressures and, in many cases, non-base metals are used.⁷ Only recently the same team reported on a pyridyl salicylimine polymeric catalyst that showed quantitative conversion without the need for additives or co-catalysts even for the conversion of hard substrates like styryl epoxide.⁸

In search for better performing solids to catalyze this reaction, the team of Yavuz discovered by serendipity the one step synthesis of a Covalent Organic Polymer (COP) with an unprecedented activity in the non-redox fixation of CO₂. COP-222 (see figure 1), an imidazolium polymer produced through the one-pot reaction of terephthalaldehyde and ammonium chloride, does not require the use of any co-catalyst, solvent or harsh reaction conditions to transform mixtures of CO₂ and a wide range of epoxides into their corresponding cyclic carbonates, including the highly sterically and electronically challenging cyclohexene oxide and resorcinol diglycidyl ether. The presence of both a slightly acidic quaternary amine and a basic amine seem to be key in the unique reactivity of COP-222. According to DFT calculations, the reaction proceeds through a nucleophilic attack driven epoxide ring opening (ND-ERO) mechanism that starts by the coordination of the epoxide to an ammonium proton followed by the activation of carbon dioxide by the resulting chloride stabilized oxyanion. In a similar fashion as Endo *et al.* reported in 1993 for different halide salts.⁹

Although it is still too early to assess the actual industrial impact that COP-222 may have, its outstanding catalytic performance, the fact that neither solvents nor co-catalysts are required, the use of commercially available polymer precursors and the one pot synthesis of the solid, they all point in the right direction. When it comes to limiting anthropogenic CO₂ emissions, such technology may be applicable, as discussed above, in small scale, remote locations. However, full life cycle analyses in the same way as it is being done for other CO₂ valorization technologies¹⁰, including derived CO₂ emissions from the production of the corresponding epoxides, should be considered when assessing the actual impact of such technology on CO₂ mitigation. Last but not least, other important points can be learned from this work: (i) in spite of the very low porosity of COP-222 (21 m²/g), catalytic activity is outstanding, (ii) this is not a crystalline solid, something certainly not needed for a reaction that does not rely on shape selectivity, yet due to the repetitive nature of polymer units, it should be considered a single site catalyst and (iii) the role of serendipity in science cannot be ignored: the authors originally speculated that the one-pot reaction of terephthalaldehyde and ammonium

chloride would form a porous material containing cyclic amines. The actual product turned out to be something else, yet something very promising.

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