**Ph.D. proposal – 2022**

# Synthesis of Vinylene Carbonates from C1 Sources

## Synthèse de carbonates de vinylène à partir de sources C1

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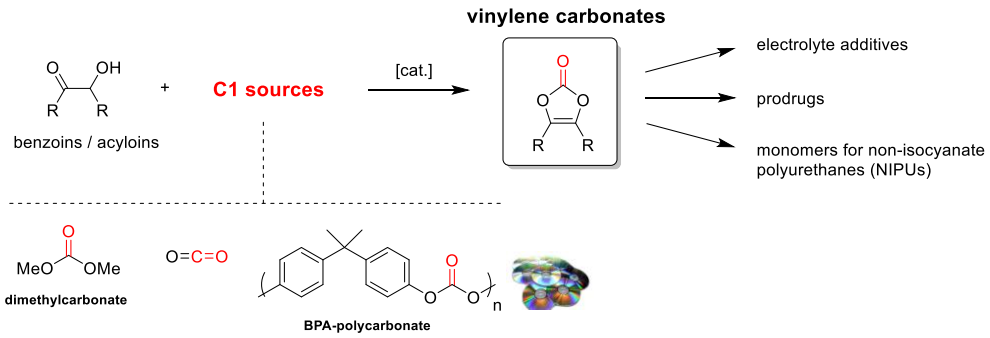
*Key-words: C1 sources ● Carbon dioxide ● Organocatalysis ● Vinylene carbonates ● Depolymerization*

**Context:** Organic carbonates are currently the subject of intense research efforts, notably due to their general innocuity and biodegradability. In this broad field, the chemistry of vinylene carbonates is considerably underdeveloped but has a significant potential in terms of applications. For example, vinylene carbonate (1,3-dioxol-2-one) can be used as an electrolyte additive in lithium batteries or as a monomer to prepare poly(vinylene carbonate), a precursor of poly(hydroxymethylene) which has found applications in 3D printing. Moreover, functionalized vinylene carbonates are key compounds to prepare medoxomil groups that are used as a cleavable function in prodrugs. Despite of these applications, the chemistry of vinylene carbonates remains undeveloped, mainly due to their limited availability linked to their problematic synthesis, involving either toxic (phosgene or triphosgene) or expensive carbonyl sources (carbonyldiimidazole, CDI).

**Previous work:** Our research activity has been recently focused on the preparation of organic carbonates from $CO_2$, notably through thermomorphic organocatalysis.[1] More recently, we have developed an organocatalytic method to prepare a wide range of vinylene carbonates from benzoins/acyloins using diphenyl carbonate as a carbonyl source.[2] This carbonylating agent is less toxic than phosgene and less expensive than CDI. However, it involves the formation of phenol as a byproduct, thus compromising the overall atom economy. In this context, more efficient synthetic routes should be developed to ensure further progress of the chemistry of vinylene carbonates.

**Ph.D. Project:** Based on our preliminary results, the aim of this Ph.D. proposal is **to develop new (organo)catalytic methods to prepare vinylene carbonates from benzoins/acyloins using various C1 sources**. First, dimethylcarbonate will be used as a safe carbonyl source that will also help to improve the atom-economy of the process. Then, carbon dioxide ($CO_2$) will also be considered to prepare vinylene carbonates. This part is the most challenging but also the most efficient as only water will be produced as a waste. Finally, we also envision that vinylene carbonates could also be prepared using waste Bisphenol A-polycarbonate as a carbonyl source, simultaneously leading to the depolymerization of this polymer (notably contained in compact disks). The recovered monomer could be used for either recycling or upcycling.




**Candidate profile:** The candidate should have a strong background in organic chemistry (M2 degree) and should be motivated to develop catalytic methods in a green chemistry context. An experience in polymer chemistry will be appreciate by not mandatory. The ability to work in a team is essential.

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[1] a) K. Grollier, N. D. Vu, K. Onida, A. Akhdar, S. Norsic, F. D'Agosto, C. Boisson, N. Duguet *Adv. Synth. Catal.* **2020**, *362*, 1696–1705 (link); b) A. Akhdar, K. Onida, N. D. Vu, K. Grollier, S. Norsic, C. Boisson, F. D'Agosto, N. Duguet, *Adv. Sustainable Syst.* **2021**, *5*, 2000218 (link).

[2] K. Onida, A. Haddleton, S. Norsic, C. Boisson, F. D'Agosto, N. Duguet, *Adv. Synth. Catal.* **2021**, *363, 5129– 5137* (link).