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EDITORIAL

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Biobased furanic derivatives for sustainable development

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The global demand for sustainable and affordable platform chemicals has been the driving force behind a fantastic breakthrough in terms of greentech innovations. In this context, biorefinery operations can produce furanic molecules, which are obtained from various constitutive sugars in biomass waste. A list of the top biobased building blocks obtained from carbohydrates has been identified as being very promising in terms of technology development and potential commercial success.

Among the biobased product portfolio, 5-hydromethylfurfural (HMF) and furfural are derived from C6 (*e.g.* fructose, glucose, …) and C5 (*e.g.* xylose) sugars, respectively. They are thus considered as seminal platform molecules for a cascade of various interesting intermediates, such as 2,5-furandicarboxylic acid (FDCA), among other carboxylic acids, as well as furfuryl alcohol, alkyl alcohols/amines, hydrocarbons, ketones, *etc*. Although furfural is now available at a large scale, this is still not the case for HMF, due to a lack of economically competitive technologies to dehydrate C6 sugars. As result, and in contrast to furfural, HMF is considered to be a sleeping giant of carbohydrate chemistry.

Based on this ascertainment, we herein propose the word "*furanery*" – as the contraction of the words *furan* and *refinery* – to further outline how important furanic molecules are in the blooming biorefining sector and the role they can play in the future of polymer technology and solvent design. Nowadays, we can really consider the value chain of furanics, and this has motivated us to propose this themed collection to enhance the latest advances in this

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broad and innovative topic, spanning from biomass conversion to derivatization and utilisation in various applications. In this line, the perspective article from Bielsky and Grynkiewicz (https://doi.org/10.1039/D1GC02402G) showed the spectacular range of compounds that can be economically synthesized from biomass *via* furan-based platform chemicals. Interestingly, the authors go beyond the broadly promoted manufacture of fuels and monomers.

From a molecular point of view, furanic molecules have multiple talents. For instance, they have both a heteroaromatic ring – providing rigidity and stability to *e.g.* polymeric chains – and they can be considered to be dienic compounds. However, some biobased furanic derivatives, such as furfural or furoic acid, have electron withdrawing substituents that will strongly limit their use as dienic compounds for Diels–Alder cycloaddition. Therefore, Bruijninckx and co-workers proposed a pathway (https://doi.org/10.1039/D1GC01535D) to circumvent the withdrawing effects from these substituents. The Diels–Alder coupling is particularly efficient when the reaction proceeds in water and is activated with a mild base to transform the carboxylic group in carboxylates, thus showcasing that these furanics can be good candidates for transformations into aromatics *via* such cycloaddition.

The catalytic transformation of furanic building blocks is an important part of this themed issue. The communication from Pomeroy *et al.* (https://doi.org/10.1039/D1GC02086B) proved that a ceria-promoted transition metal catalyst can promote very high selectivity to reach important yields of key polyfunctional alcohols from HMF hydrogenation. In the same vein, Liang *et al.* (https://doi.org/10.1039/D1GC01286J) showed that a non-noble metal catalyst over graphitic carbon nitride is able to completely convert (with very high selectivity) HMF into 2,5-diformylfuran *via* photocatalytic dehydrogenation. A multicatalytic route was proposed by the group of Thomas (https://doi.org/10.1039/D1GC01889B) to get access, in one-pot, to 2,5-bis(hydroxymethyl)furan and the ensuing polyesters, also incorporating FDCA, using several commercial catalysts.

Electrocatalysis is an interesting alternative to chemical or enzymatic catalysis when the objective is to further derivatize furanic building blocks. Gouda *et al.* (https://doi.org/10.1039/D1GC02031E) demonstrated that HMF can be efficiently converted into FDCA using a nickel-based electrocatalyst. The chemical selectivity is over that of the competing oxygen evolution reaction provided that the electrolyte solution does not contain iron impurities.

The application of furanic derivatives to the preparation and application of sustainable and functional materials is another prominent topic in this collection. FDCA based polyesters have been in the spotlight for a decade, in particular poly(ethylene 2,5-furanoate) – PEF. However, most of the PEF syntheses have, so far, focused on the transesterification of dimethyl FDCA with ethylene glycol. The group of Bikiaris (https://doi.org/10.1039/D0GC04254D) proposed a detailed investigation into the multi-step kinetics of direct FDCA esterification and polycondensation, leading to PEF. The originality of this work is that several structural and physico-chemical approaches have been employed (including the use of high-resolution mass-spectrometry for determination), complemented with theoretical investigations.

Considering thermoset applications, Tellers *et al.* (https://doi.org/10.1039/D0GC04323K) proposed a new furfural based cyclobutane diacid for being employed as a crosslinking agent for biobased epoxy resins. The mechanical properties offered by this biobased furanic crosslinker surpass those of other biobased alternatives (*e.g.* natural diacids) and compete well with petroleum based hardeners (*e.g.* aromatic amines, *etc.*) that urgently require more sustainable (and less toxic) alternatives.

Furfuryl alcohol is an interesting furanic monomer that can be impregnated into wood cells to create – upon thermal curing – a polyfuranic network. This process, called furfurylation, allows the fabrication of durable wood. Thygesen and co-workers (https://doi.org/10.1039/D1GC01524A) shed new light on furfurylation and particularly its impact on the biodegradation process of wood timber in marine environments. They analysed the behaviour of the gribble (a marine crustacean that causes the main biodeterioration of timber in the sea). They concluded that furfurylation increases the hardness of wood and disrupts the enzymatic digestion from the gribble, thus resulting in the long-lasting protection of wood.

Finally, Sousa *et al.* (https://doi.org/10.1039/D1GC02082J) have written a tutorial review to guide researchers and stakeholders on the potential (current and future) sustainable alternatives to replace PET. Indeed, this polyester, which counts for 7.7% of the global plastic share, has promising alternatives among the furan-based polymers family. This review also explores the end-of-life options of the foreseen sustainable alternatives.

As guest editors of this themed issue, we would like to thank all the authors for the high quality of their contributions and the appealing conclusions and perspectives of their investigations. This themed collection aims to pave the way to an increased knowledge of furanic derivatives and their potential for sustainable applications in various sectors. This collection should also further stimulate the engagement of multiple stakeholders gravitating around the field of *furanery*.

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