EDITORIAL

Synthetic Electrochemistry

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Synthetic organic electrochemistry offers a number of advantages over traditional chemical synthesis, potentially circumventing the need for the addition of toxic, hazardous and expensive reagents by driving reactivity through the manipulation of electrons(ref). In recent years, the field has undergone a remarkable resurgence, which can be attributed to a number of factors: (1) the availability of standardised commercially available reactor technology, from high-throughput experimentation, to batch and flow reactors(ref); (2) a broader understanding of the field, through the outstanding work of a number of chemists to deconvolute and provide critical overviews of the literature, whilst also developing guides to non-experts in the field(ref); (3) an influx of new researchers to the field, keen to harness the power this technology to drive new discoveries.

This rapid growth in the popularity of synthetic electrochemistry has brought numerous advances, not only in the identification of improved and more sustainable conditions for known reactions, but also in the ability to harness electrons to access new chemical space. Through both of these paradigms, significant advances have been made in numerous fields, including the total synthesis of natural products, the synthesis of materials, functionalisation of biomolecules, and in pharmaceutical and agrochemical synthesis.

We are delighted to present this Themed Collection in *Organic & Biomolecular Chemistry* on *Synthetic Electrochemistry*, covering key advances in the field, including the development of new synthetic methods, and reviews which will be of interest to the both those experienced in synthetic electrochemistry, and those looking to develop their understanding of the field.

Electrochemical methods have proven their utility in the synthesis of natural products since Corey's synthesis of pentacyclosqualene in 1958(ref). Munda and coworkers (DOI: 10.1039/D1OB02115J) provide a holistic overview of the application of electrochemistry in the synthesis of a range of complex alkaloids. Further advances to this field are presented by Shaw and coworkers (DOI: 10.1039/D1OB01463C) who present an electrochemical proton-coupled electron transfer for the dimerisation of oxindoles in the total synthesis of (±)-folicanthine.

Halogens provide key functional handles across synthetic chemistry, Scheide and coworkers (DOI: 10.1039/D0OB02459G) present a comprehensive review of electrochemical methods for introduction of sp^2 and sp^3 fluorine, chlorine, bromine and iodine substituents. Seitz and Wirth (DOI: 10.1039/D1OB01302E) demonstrate bromofunctionalisation of alkenes utilising the anodic oxidation of HBr to circumvent the need for Br_2 or stoichiometric oxidations. This work highlights the utility of flow chemistry in facilitating the handling of reactive species, and in enabling further scale up. Elsherbini and Moran (DOI: 10.1039/D1OB00457C) report the synthesis of unsymmetrical cyclic and acyclic diaryliodonium salts by anodic oxidation, obviating

the need for stoichiometric chemical oxidants, with a scalable procedure which benefits from a recyclable solvent system.

Functional group transformations are key steps in many synthetic routes, and electrochemistry can provide both alternative and more sustainable options to these, alongside opening up previously inaccessible disconnections. Chen and coworkers (DOI: 10.1039/D1OB00420D) highlight the range of possible decarboxylative electrochemical functionalisations in their review on recent progress in electrochemical synthesis involving carboxylic acids. The reduction of benzoic acids to cyclohexane carboxylic acids typically requires the use of stoichiometric metal reductants or expensive catalysts. Fukazawa and coworkers (DOI: 10.1039/D1OB01197A) report a method utilising a PtRu cathode for the electrocatalytic reduction of benzoic acids in a proton-exchange membrane reactor. Chang and coworkers (DOI: 10.1039/D1OB00077B) report a scalable chemoselective reduction of nitroarenes with gaseous ammonia as a reductant to afford azoxybenzenes, azobenzenes, hydrazines and anilines *via* stepwise cathodic reduction. Zhang and coworkers (DOI: 10.1039/D0OB02444A) report a novel electrochemical alternative to the Darzens condensation, through a peroxide-free oxidative coupling of ketones and aldehydes mediated by potassium iodide, to furnish α,β-epoxy ketones.

New disconnections for the synthesis of heterocycles, and access to previously unexplored chemical space is of paramount importance in the development new medicines and agrochemicals. Hou and coworkers (DOI: 10.1039/D1OB01644J) utilise a novel tetraarylhydrazine mediator in an intramolecular {3+2} heteroannulation to access imidazo-fused bicyclic heteroaromatics, a key component of a number of marketed pharmaceuticals. Zhang and coworkers (DOI: 10.1039/D1OB00079A) have developed an oxidant-free, cascade radical synthesis of 3-sulfonylated benzothiophenes *via* anodic oxidation of sulfinate salts from readily available 2-alkynyl thiophenol derivatives. Further demonstrating the benefits of continuous flow technology in electrochemical synthesis, Bian and coworkers (DOI: 10.1039/D1OB00236H) present a novel disconnection for the synthesis of selenium-substituted iminoisobenzofurans.

The application of synthetic electrochemical techniques to the synthesis and functionalisation of biomolecules is a rapidly expanding area. Stricker and coworkers (DOI: 10.1039/D1OB00414J) report the modular synthesis of foldable flavin-peptide conjugates and investigate both the folding and redox characteristics of the conjugate, opening up potential future avenues for asymmetric catalysis and electrode functionalisation.

As is made evident by the range of articles in this Themed Collection, synthetic electrochemistry has applications across a remarkable breadth of scientific endeavours. We are grateful to all the authors for their contributions to their collection, and are excited and optimistic for the future growth of synthetic chemistry, the opportunities it will continue to provide to streamline the synthesis of functional molecules, and open up exciting new areas of chemical space.

Notes and references

1 Citations should appear here in the format A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523; A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523.
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