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EDITORIAL

Proton-coupled electron transfer

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Association between proton and electron transfer is omnipresent in chemistry, biology as well as in catalysis. The interest for these proton-coupled electron transfers (PCET) reactions stems from the fact that they play a key role in all the processes leading to energy storage into chemical bonds, and thus for all expected renewable energy systems based on solar fuels. Multiple proton-coupled electron transfers involved, *e.g.* in carbon dioxide reduction, in water oxidation as well as in hydrogen evolution from acids, are already of crucial importance in the design of catalytic processes with the aim of tackling contemporary energy challenges. Although some catalysts—either homogeneous or heterogeneous, bio-inspired or not, based on earth abundant materials—have been designed and tested for the above mentioned complex transformations, it is unlikely that any "screening strategy" will lead to the development of cheap, efficient, durable and easily scalable catalytic systems.

The difficulties and complexities of these 21st century chemistry holy grails are not only due to the necessity of carrying out multiple proton–electron transfers and proton transport while maintaining high efficiency, but are also a consequence of associating proton-coupled electron transfer to bond breaking or forming between heavy atoms, *e.g.*, C–O cleavage during CO_2 reduction or O–O bond formation during water oxidation. Various transition metal catalysts have been explored but it is clear that many more fundamental, theoretical and mechanistic studies are necessary to understanding the intrinsic and extrinsic parameters that control the kinetics, thermodynamics and efficiency of the overall catalytic cycle. Recent advances and understanding, through various experimental examples of concerted proton–electron transfers that skip the high energy intermediates involved in the stepwise pathways certainly stimulated the interest for these classes of reactions and opened new ways of thinking that will in turn be useful for designing efficient catalysts. Coming from the many corners of physical, organic and bio-inspired chemistry, the collection of articles gathered in this special issue mirrors the diversity of approaches towards these fundamental studies as well as the massive interest of the chemists for PCET reactions.

This issue originates from the first international (PCET 2011 – "From Biology to Catalysis"), EES co-sponsored meeting dedicated to all aspects of PCET reactions, from biology, biochemistry and DNA to spectroscopy and theoretical aspects, through catalysis and small molecules activation, that has been held last October in France. The success of this meeting reflects the flourishing and diverse activity in the field and will likely stimulate innovative studies based on rational, mechanistic, and both experimental and theoretical, approaches.

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