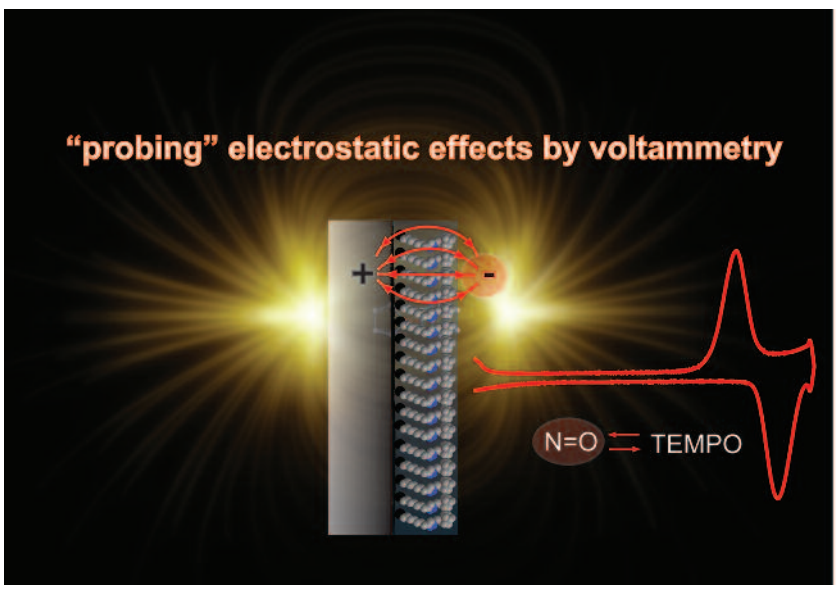
Controlling electroactivity of surface-tethered radicals

Cyclic voltammetry is a well-established form of electrochemical 'spectroscopy' that yields a great wealth of mechanistic and thermodynamic information from the analysis of a current flowing across an electrified interface. A team of researchers from the University of Wollongong, the Australian National University, the University of New South Wales, Institut de Bioenginyeria de Catalunya and ANSTO has used this technique to show how a seemingly simple 'dynamic' current–potential trace can yield quantitative insights into the 'electrostatic' environment around a surface-tethered nitroxide radical (Zhang L., Vogel Y.B., Noble B.B., Gonçales V.R., Darwish N., Le Brun A., Gooding J.J., Wallace G.G., Coote M.L., Ciampi S. *J. Am. Chem. Soc.* 2016, **138**, 9611–9). The level of doping and nature of the electrolyte were found to cause drastic kinetic changes to the electroactivity of the radical monolayer as well as electrochemical non-idealities. Calculations indicate that these unusual effects are electrostatic in origin and arise from interactions between the nitroxide radical (2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO)) and either electrolyte species or ionised dopants in the semiconducting electrode. This work has important implications for how charged groups or externally applied electric fields can influence chemical bonding and reactivity, an area that is beginning to attract enormous interest (see, for example, Aragonès A.C. et al., *Nature* 2016, **531**, 88–91).



Compiled by **David Huang** MRACI CChem (david.huang@adelaide.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high impact journals (e.g. *Nature*, *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.*) are encouraged to contribute general summaries, of no more than 200 words, and an image to David.