Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supporting Information for

Harnessing Electrostatic Catalysis in Single Molecule, Electrochemical and Chemical Systems: A Rapidly Growing Experimental Tool Box

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S1. Near-surface electric fields at electrode/electrolyte interfaces.

The electrode surface holds a charge density which arises either from an excess or deficiency of electrons. Charges on an electrode establish a potential difference with respect to the bulk solution need to be compensated by an excess of ions of the opposite charge. The distance at which the ions can approach the electrode surface is limited to the radius of the ion and a layer of solvation around each ion. This leads to two layers of charge and hence the term double layer. Models describing the structure of the electrical double layer date from the 1850s. Today, the most commonly used model is the Gouy−Chapman−Stern one which defines the region between the surface of the electrode and the locus of the first hydrated counter-ions as the Stern layer across which there is a linear drop in potential. After the Stern layer there is the diffuse layer, or the Gouy−Chapman layer which displays an approximately exponential decay in potential out to the bulk electrolyte according to the Poisson−Boltzmann equation and later by the Debye-Huckel equation which takes into account interaction energy of ions in the solution.

Electrochemists appreciate that for the ionic conduction in a liquid to become electronic conduction in a solid, a diffusive molecule has to approach or cross the electric double layer of charges at the solid/liquid interface. What evidence points to existence of this double layer? A novice electrochemist has often to be reminded of paying attention to two steps: 1) that when interpreting experimental electrochemical data it is necessary to carefully choose a baseline against which the “interesting” faradaic current has to be measured, and 2) to add an excess of “uninteresting” salt support. The excess of supporting electrolyte screens the bulk from electric fields preventing migration to contribute significantly to mass transport so that simple diffusion-only theories based on Fick’s laws are then applicable.

Regarding the first point, a voltammetric current it is seldom zero, even in the absence of a redox-active species. The oxidation/reduction current change with the concentration of the “interesting” analyte, but what is the physical origin of the capacitive background signal? The charge applied by a potentiostat to a working electrode changes its Fermi level. By using an ideal reference electrode any change to the potential difference between reference and working electrode will translate exactly into the same potential difference change between the working and the bulk electrolyte solution. As the potential is changed, ions in solution moves without them being either oxidised or reduced, and in fact the potentiostat records a measurable current even in the absence of electrolysis (i.e. no net chemical change). In other words, charges on the electrode that establish a potential difference with respect to the bulk solution need to be compensated by an excess of ions of the opposite charge, something akin to a double layer of charges (Figure 6, main text).

As discussed in the main text, salting-out of colloidal particles is a text-book example that is often used to make a reality out of this otherwise abstract concept of a double layer.[1] Ions around the surface are subject to thermal diffusion and hydrodynamic drag creating a "cloud" of counter-ions above the surface known as the electrical double layer, or Debye layer. The salting-out occurs when the “reach” of electrostatic forces is short of then colloidal particles have a greater chance of colliding against each other, hence coagulating and drop out of solution. A second illustrative example is corrosion. Anodic dissolution of a metal by itself cannot occur “uncoupled” to a second redox process, often oxygen reduction, for any length of time. This would lead to charging of the metal to a high negative potential. The engineering rule-of-thumb limit of 6 ng of iron for a hypothetical “uncoupled” corrosion, corresponding to *ca*. 10^{-10} mol of iron, is just a reflection of an approximate double layer capacitance of 20 mF cm^{-2}. It takes 20 mC of charge for the potential across the interface to reach an opposing 1 V, and this is the *ca*. 10^{-10} mol of dissolved iron.

S2. Supplementary Figures

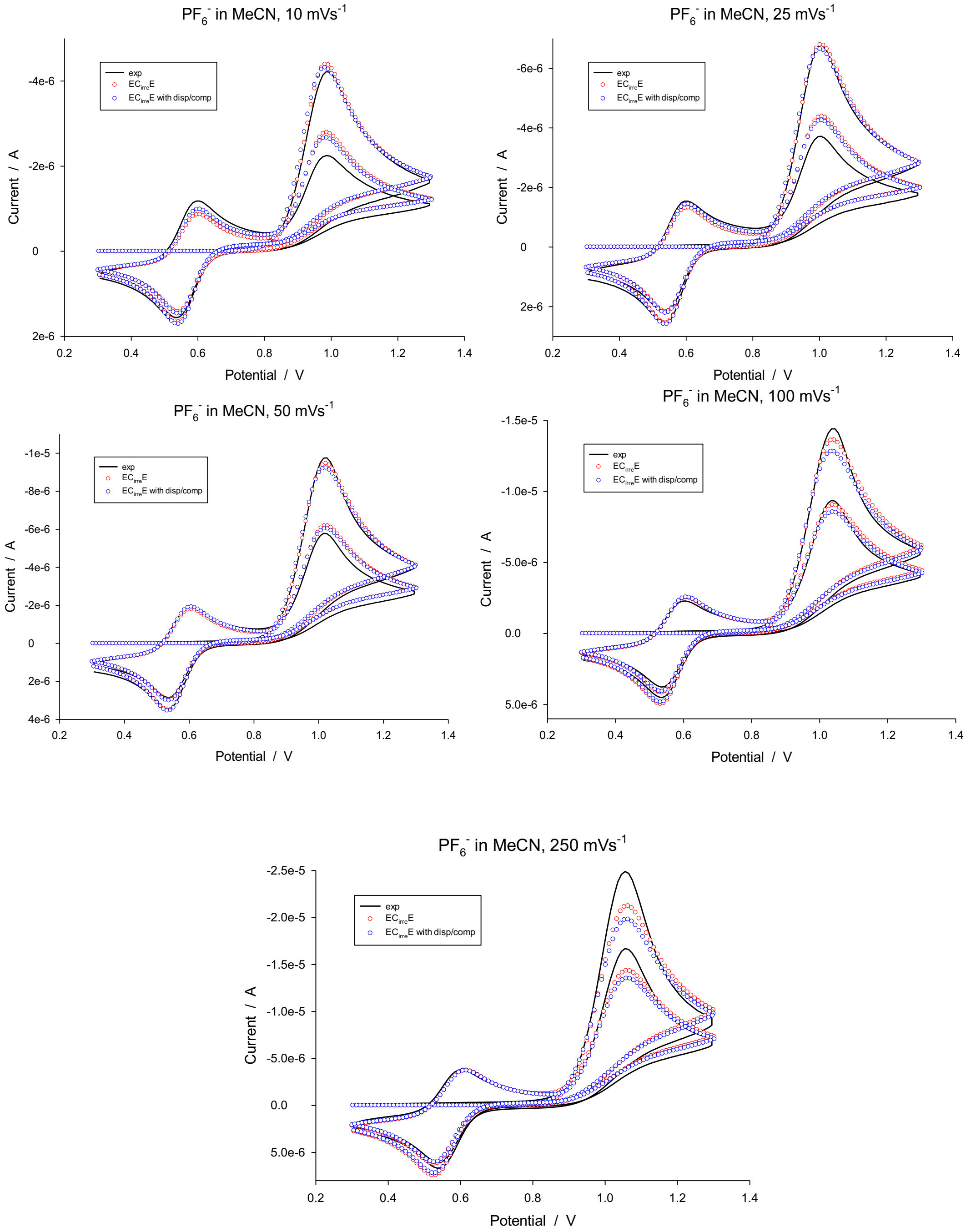

Figure S1. The complexity of ECE processes is such that one cannot immediately rule out the possibility of a DISP/COMP contribution. We did analyse our published voltammetry[2] to include for a DISP-COMP pathway and above are representative data (cyclic voltammograms of 0.5 × 10^{-3} M of the alkoxyamine in Figure 9 of the main text, MeCN/Bu_4NPF_6) and simulations based on a theoretical treatment reported recently on this specific subject (Á. Molina, E. Laborda, J.M. Gómez-Gil, F.

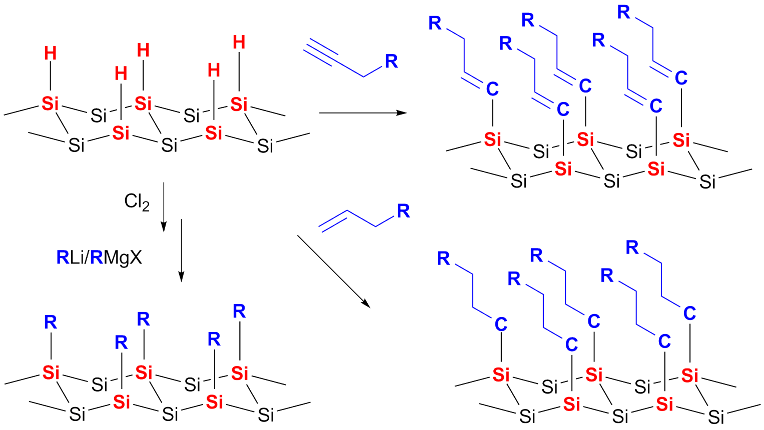

Figure S2. Surface-assembly at macroscopic electrodes/electrolytes interfaces by wet chemistry. Hydrosilylation of unsaturated molecules and alkylation of halide-terminated surfaces. The reaction is most commonly initiated using heat or UV/white light (although other approaches are also employed) to link the alkyl chains to the substrate by a Si–C bonds.[3-5] Hydrogen-terminated crystalline silicon are first etched in aqueous fluoride solutions, surfaces will then be transferred to an oxygen-free Schlenk line environment where they are reacted with samples of either internal alkenes (e.g. norbornyl bridges[6]), 1-alkynes[4] (1,8-nonadiyne in Figure 1o of the main text) or 1-alkenes.[7] The functionalization of the Si–H surface results in a stable Si–C, covalent bond, and organic monolayers of exceedingly high capacitance, where direct electrical communication between the grafted molecule and the substrate is still possible.[8]

Martínez-Ortiz, R.G. Compton, *Comprehensive Voltammetric Characterisation of ECE Processes*, Electrochim. Acta, 195 (2016) 230). Including the possibility of DISP/COMP does not improve our published mechanistic results, and similar fittings are obtained (see plots above). In brief, DISP-COMP was not found to affect our published conclusions[2] on a simple ECE mechanism in a significant way. DISP/COMP pathways ($K_{\mathrm{DISP/COMP}}$ set to 2.0 × 10^7).

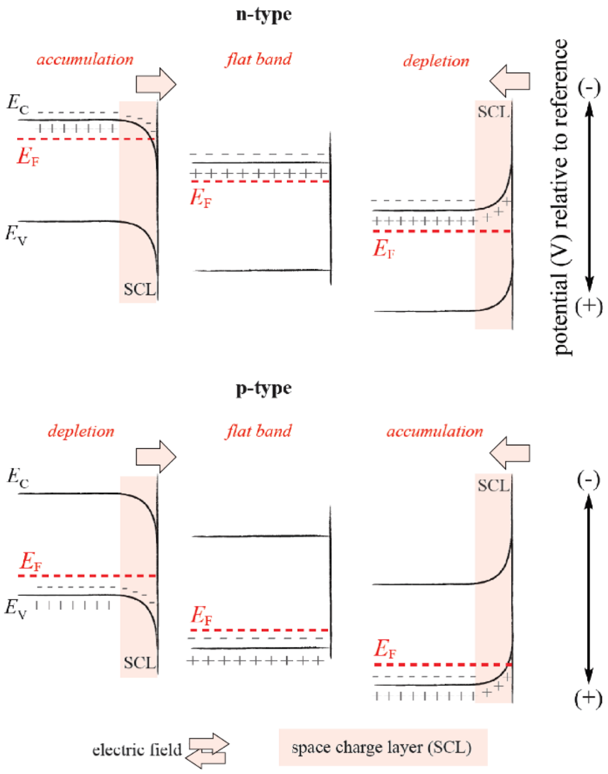

Figure S3. Effect of bias V ($V < V_{FB}$, $V = V_{FB}$, $V > V_{FB}$, from right to left) on the band diagram for n- and p-type electrodes (top and bottom panels).

S3. References

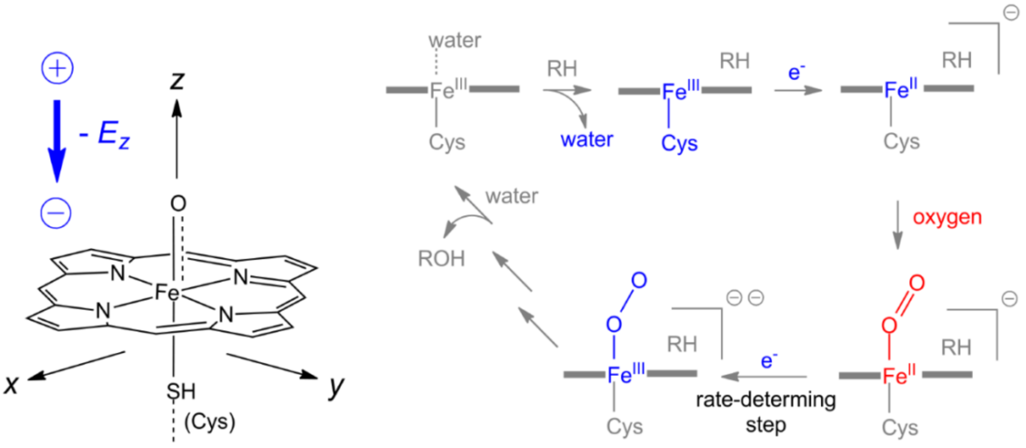

Figure S4. *Switching on* and *switching off*; acceleration/retardation EEFs effects on the catalytic cycle of cytochrome P450 (CYP).[9] EEF oriented along the negative *z*-direction will facilitate the displacement of the water ligand and will facilitate two reduction steps, but will obstruct oxygen binding. The net EEF effect is an increased efficiency of the catalytic cycle. Reversing the EEF direction is predicted *turn off* the cycle.

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