

**P029** Tuning the heme redox potential in the cytochrome  $c_6$  family

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Cytochrome  $c_{6A}$  is a unique dithio-cytochrome of green algae and plants. It has a very similar core structure to that of bacterial and algal cytochromes  $c_6$  but is unable to fulfil the same function of transferring electrons from cytochrome  $f$  to photosystem I. A key feature is that its heme mid-point potential is more than 200 mV below that of cytochrome  $c_6$  ( $E_m \sim +340$  mV) despite having His and Met as axial heme-iron ligands. One salient difference between the heme pockets is that a Val in cytochrome  $c_{6A}$  replaces a highly conserved Gln in cytochrome  $c_6$ . This difference has been probed using site-directed mutagenesis, X-ray crystallography, protein film voltammetry and equilibrium unfolding studies. It is found that the stereochemistry of the Gln within the heme pocket has a destabilizing effect and is responsible for tuning the hemes mid-point potential by over 100 mV. This large effect has consequences in facilitating a new function for cytochrome  $c_{6A}$ .