Experimental Procedures.

PFV was performed and analyzed as described in Gwyer *et al.* Biochemistry 2004, 43, 15086-15094 with the exception that a) films were prepared from a solution containing 0.16 μM cytochrome *c* nitrite reductase and b) a buffer-electrolyte of 2 mM $CaCl_2$ and 10 mM each of Hepes, Taps, Mes and Acetate was employed. Variation of the catalytic current at –0.6 V with nitrite concentration confirmed that 1 μM nitrite was well below the K_M at each pH. The catalytic current-potential profiles were indistinguishable for scan rates between 5 and 100 mV s^{-1} with an electrode rotation rate of 3000 rpm for each pH investigated. For Figures that include error bars these represent one standard deviation of the mean of five measurements.

Figure S1. Variation of half-height width of features in first derivatives of catalytic current with respect to applied potential. Circles; negative feature in the derivative. Squares; positive feature in the derivatives. The broken lines indicate the values expected for n = 1 and n = 2 processes at the temperature of the experiments.

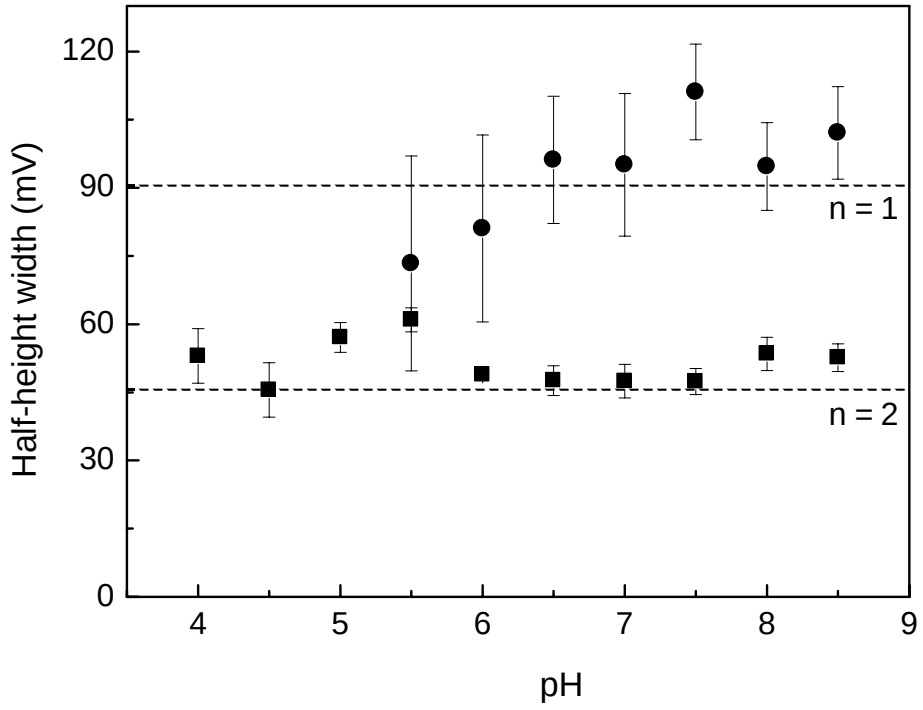

Figure S2. Variation of E_{cat} and E_{atten} with electrode rotation rate at pH 4, 6 and 9 as indicated.

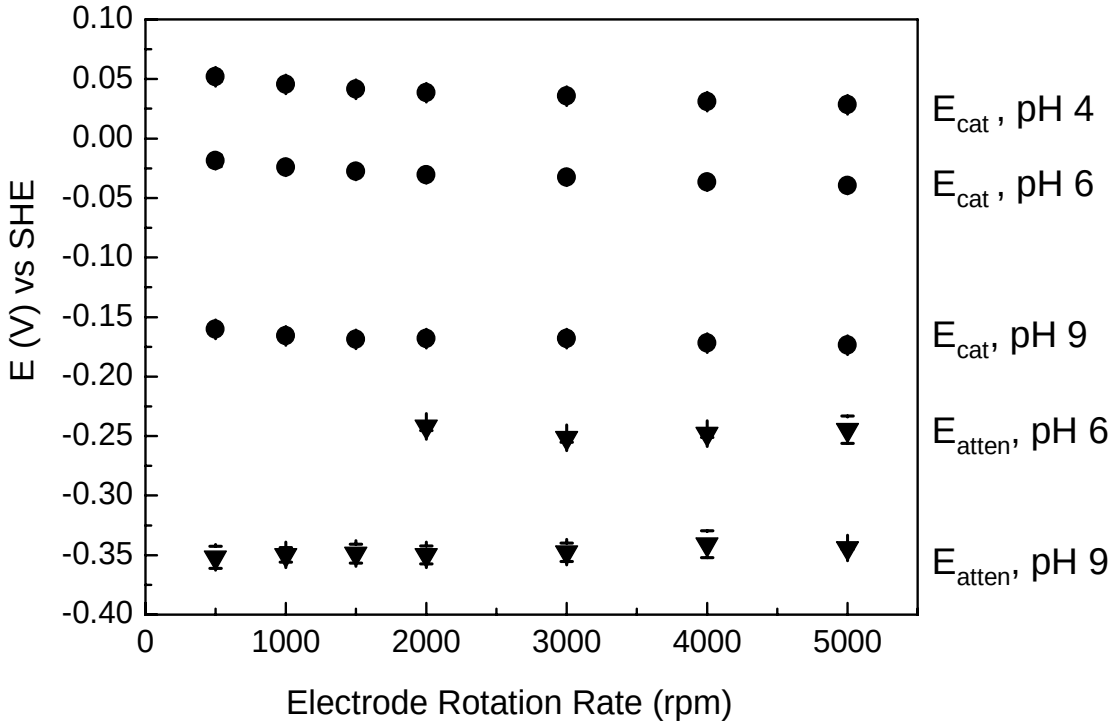

Figure S3. *E. coli* cytochrome *c* nitrite reductase highlighting the hemes and amino acids discussed in the manuscript. For one monomer the main chain is shown in ribbon form.
Blue: the spin-coupled heme pair identified by EPR spectroscopy ($E_{m,7}$ –107 mV).
Green: hemes that may give rise to the large g-max signal identified by EPR spectroscopy ($E_{m,7}$ –323 mV).
Yellow: heme giving rise to rhombic EPR signal ($E_{m,7}$ -37 mV).
Black: His 388 and His391. Red: Arg106, His227 and Tyr179.
Grey: amino acids that form heme axial ligands.
For details see Bamford *et al. Biochemistry* **2002**, *9*, 2921-2931. Figure drawn in Rasmol from PDB entry 1GU6.