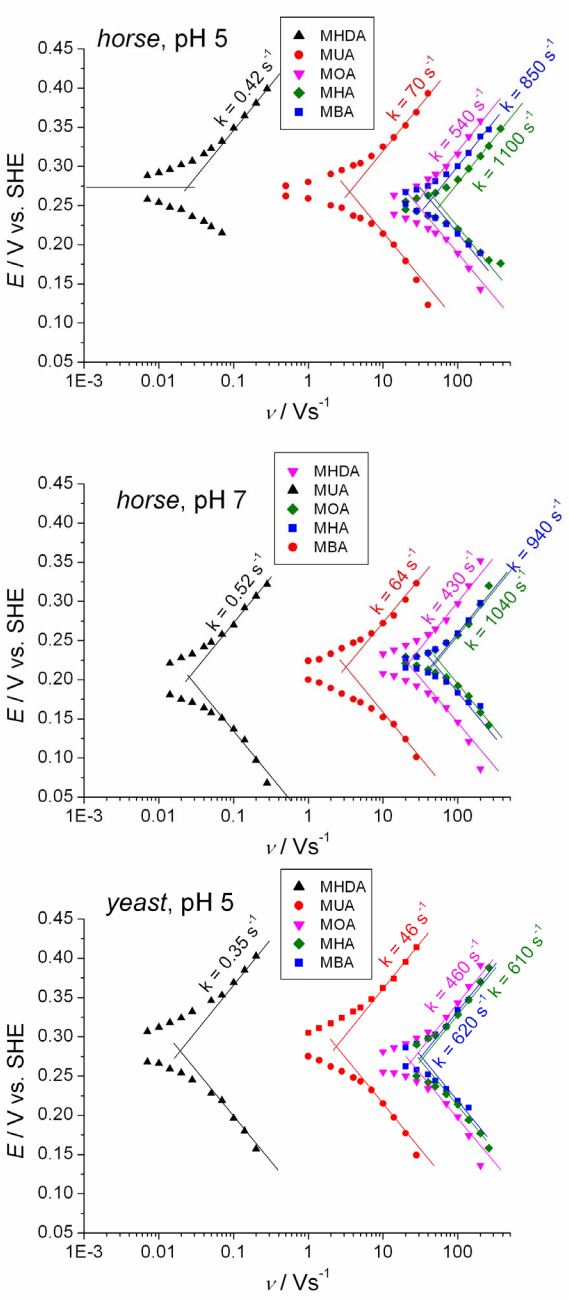
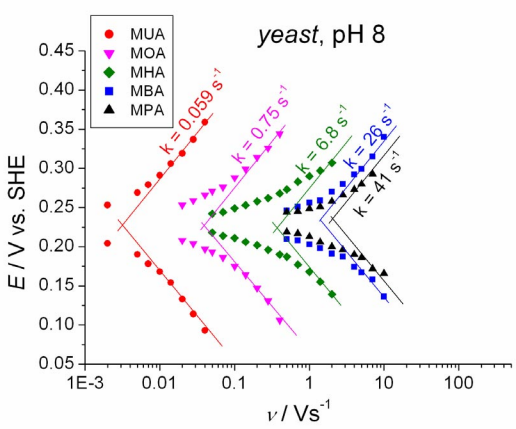
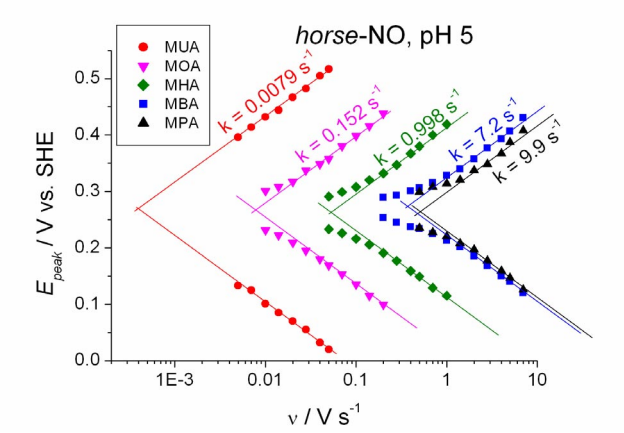
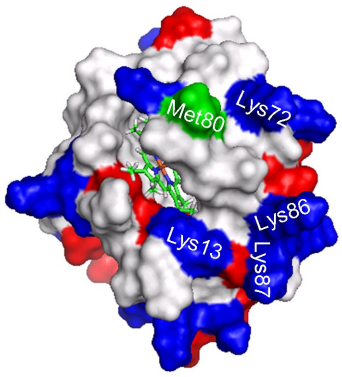

horse, pH 5
MHDA
MUA
MOA
MHA
MBA
k = 0.42 s-1
k = 70 s-1
k = 540 s-1
k = 850 s-1
k = 1100 s-1
E / V vs. SHE
ν / Vs-1
horse, pH 7
MHDA
MUA
MOA
MHA
MBA
k = 0.52 s-1
k = 64 s-1
k = 430 s-1
k = 940 s-1
k = 1040 s-1
E / V vs. SHE
ν / Vs-1
yeast, pH 5
MHDA
MUA
MOA
MHA
MBA
k = 0.35 s-1
k = 46 s-1
k = 460 s-1
k = 610 s-1
k = 620 s-1
E / V vs. SHE
ν / Vs-1



S1. Trumpet plots for *horse* and *yeast* cytochrome *c* immobilized on gold with a SAM of 3-mercapto propionic acid (MPA), 4-mercaptobutyric acid (MBA), 6-mercaptohexanoic acid (MHA), 8-mercaptooctanoic acid (MOA), 11-mercaptoundecanoic acid (MUA) or 16-mercaptohexadecanoic acid (MHDA). Cathodic and anodic peak potentials were determined from voltammograms that were recorded in either 10 or 50 mM acetate, pH 5.0 or 10 or 50 mM phosphate, pH 7.0 containing 400 nM cytochrome *c* at scan rates ranging from 2 mV s^{-1} to 300 V s^{-1}. Peak potentials were corrected for ohmic drop at high scan rates. High scan rate measurements of cytochrome *c* on SAMs of MOA, MHA, MBA and MPA were performed in a 50 mM acetate or 50 mM phosphate solution to avoid large ohmic drops. This does not affect the rate constants, as was evidenced by values of 70 s^{-1} and 75 s^{-1} for *horse* cytochrome *c* on MUA in respectively 10 mM and 50 mM acetate.



S2. Trumpet plots for *yeast* cytochrome *c* immobilized on gold with a SAM of MPA, MBA, MHA, MOA, MUA or MHDA in saturated NO solution. Cathodic and anodic peak potentials were determined from voltammograms that were recorded in 10 mM acetate, pH 5.0 containing 200 nM cytochrome *c* at scan rates ranging from 2 mV s^{-1} to 300 V s^{-1}. Peak potentials were corrected for ohmic drop at high scan rates. The corresponding electron transfer rate constants, which were calculated using Laviron's theory are also reported.



S3. Charge distribution on cyanide bound *horse* cytochrome *c* at pH 7. Positive groups (lysine and arginine) are depicted in blue, whereas negative groups (aspartic acid and glutamic acid) are depicted in red. Methionine 80 has been depicted in green for

accentuation. The heme groups are depicted as sticks in green. Prepared with PyMOL. PDB codes: 1I5T