

Cover Page



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## List of abbreviations and symbols

|                 |  |
|-----------------|--|
| [xFe-yS]        | Iron-sulfur cluster  |
| 9-BBN           | 9-Borabicyclo(3.3.1)nonane                                     |
| A               | Electrode surface area [m <sup>2</sup> ]                       |
| AcOH            | Acetic acid  |
| AcSH            | Thioacetic acid  |
| $\alpha$        | Electron transfer coefficient                                  |
| ATP             | Adenosine triphosphate   |
| $\beta$         | Decay constant [ $\text{\AA}^{-1}$ ]                           |
| Bis-Tris        | 2-[Bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)propane-1,3-diol |
| calcd.          | Calculated   |
| CAN             | Ceric ammonium nitrate   |
| cat.            | Catalytic (amount)   |
| CE              | Counter electrode  |
| d               | Doublet (NMR)  |
| DCAD            | Di-(4-chlorobenzyl)-azodicarboxylate                           |
| DCM             | Dichloromethane  |
| dd              | Double doublet (NMR)   |
| DEAD            | Diethyl azodicarboxylate                                       |
| DEAE            | Diethyl aminoethanol   |
| $\delta$        | Chemical shift   |
| $\Delta E_p$    | $E_{pa} - E_{pc}$ [V]  |
| DIBAL-H         | Diisobutylaluminium hydride                                    |
| DMA             | Dimethylacetamide  |
| DMF             | Dimethylformamide  |
| Dms(A-C)        | DMSO reductase subunit   |
| DMS             | Dimethyl sulfide   |
| DMSO            | Dimethyl sulfoxide   |
| dt              | Double triplet (NMR)   |
| $E$             | Applied potential [V]  |
| <i>E. coli</i>  | <i>Escherichia coli</i>  |
| $E^{o'}$        | Equilibrium (midpoint) potential [V]                           |
| $E_i^{o'}$      | Microscopic equilibrium potential [V] (PCET model)             |
| EDTA            | Ethylenediaminetetraacetic acid                                |
| $E_p, E_{peak}$ | Peak position [V]  |
| $E_{pa}$        | Anodic peak position [V]                                       |
| $E_{pc}$        | Cathodic peak position [V]                                     |

|                         |   |
|-------------------------|---|
| $E^Q/E^{SQ}$            | Midpoint potential of quinone/semiquinone redox pair [V]                                  |
| $E^{SQ}/E^{QH2}$        | Midpoint potential of semiquinone/quinol redox pair [V]                                   |
| Et <sub>3</sub> N       | Triethylamine   |
| EtOAc                   | Ethyl acetate   |
| EtOH                    | Ethanol   |
| $F$                     | Faraday constant (96485... C/mol)   |
| FAD                     | Flavin adenine dinucleotide   |
| Fc                      | Ferrocene   |
| Frd(A-D)                | Fumarate reductase subunit  |
| FWHM                    | Full width at half maximum  |
| $\Gamma$                | Surface coverage  |
| h                       | Hour(s)   |
| HEPES                   | 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid                                   |
| His <sub>6</sub>        | Polyhistidine tag of length six   |
| HQ                      | Hydroquinone  |
| HQNO                    | N-oxo-2-heptyl-4-hydroxyquinoline   |
| HR-MS                   | High resolution mass spectrometry   |
| $i$                     | Current [A]   |
| $I$                     | Ionic strength  |
| $i_{cat}$               | (Maximum) enzymatic catalytic current [A]   |
| $i$ -PrOH               | Isopropanol   |
| $J$                     | Coupling constant [Hz]  |
| $k_0$                   | Standard rate constant (Butler-Volmer kinetics) [ $s^{-1}$ ]                              |
| $k_{app}$               | Apparent electron transfer rate constant [ $s^{-1}$ ]                                     |
| $k_{cat}$               | Apparent unimolecular rate constant/turnover number [ $s^{-1}$ ]                          |
| $k_{enz}$               | Catalytic (enzymatic) rate constant [ $s^{-1}$ ]  |
| $K_M$                   | Michaelis constant [M]  |
| $k_s$                   | Microscopic 'pure-electron' rate constant [ $s^{-1}$ ]                                    |
| KSAC                    | Potassium thioacetate   |
| $\lambda$               | Reorganization energy [eV]  |
| $\lambda_{max}$         | Wavelength at maximum absorbance [nm]   |
| LB                      | Lysogeny broth  |
| m                       | Multiplet (NMR)   |
| $m/z$                   | Mass-to-charge ratio  |
| <b>M</b> <sub>0-3</sub> | Menaquinone-terminated OPV-based molecular wire;<br>number indicates length of OPV system |
| MeOH                    | Methanol  |
| min                     | Minute(s)   |
| MK/MKH <sub>2</sub>     | Menaquinone/menaquinol  |
| MOPS                    | 3-Morpholinopropane-1-sulfonic acid   |

|                        |  |
|------------------------|--|
| MQ/MQH <sub>2</sub>    | Menaquinone/menaquinol   |
| <i>n</i>               | Number of electrons participating in a redox process   |
| <i>N<sub>A</sub></i>   | Avogadro constant (6.022... × 10 <sup>23</sup> mol <sup>-1</sup> )   |
| NADH                   | Nicotinamide adenine dinucleotide  |
| <i>n<sub>app</sub></i> | Apparent number of electrons participating in a redox process  |
| NBu <sub>3</sub>       | Tributylamine  |
| <i>n</i> -BuLi         | <i>n</i> -Butyllithium   |
| NHE                    | Normal hydrogen electrode  |
| NMe <sub>3</sub>       | Trimethylamine   |
| NMR                    | Nuclear magnetic resonance (spectroscopy)  |
| norm.                  | Normalized   |
| OPV                    | Oligo(phenylenevinylene)   |
| PCET                   | Proton-coupled electron transfer   |
| PCR                    | Polymerase Chain Reaction  |
| Pd(OAc) <sub>2</sub>   | Palladium (II) acetate   |
| PET                    | Petroleum ether  |
| PFV                    | Protein film voltammetry   |
| PIFA                   | (Bis(trifluoroacetoxy)iodo)benzene   |
| <i>pK<sub>ai</sub></i> | Microscopic acid dissociation constant (PCET model)  |
| PMSF                   | Phenylmethane sulfonyl fluoride  |
| PPh <sub>3</sub>       | Triphenyl phosphate  |
| ppm                    | Parts per million  |
| q                      | Quartet (NMR)  |
| Q/QH <sub>2</sub>      | (Ubi)quinone/(ubi)quinol   |
| Q <sub>H</sub>         | High-affinity (ubi)quinone binding site of cytochrome <i>bo</i> <sub>3</sub>   |
| Q <sub>L</sub>         | Low-affinity (ubi)quinone binding site of cytochrome <i>bo</i> <sub>3</sub>  |
| Q-wire                 | Ubiquinone- or menaquinone-terminated OPV-based molecular wire, functionalized with a gold electrode-binding thiol at the opposite end |
| <i>R</i>               | Gas constant (8.3145... J mol <sup>-1</sup> K <sup>-1</sup> )  |
| RE                     | Reference electrode  |
| <i>R<sub>G</sub></i>   | Radius of gyration   |
| <i>ρ</i>               | Electrode surface roughness factor   |
| rpm                    | Rotations per minute   |
| RT                     | Room temperature (298 K)   |
| s                      | Singlet (NMR)  |
| SAM                    | Self-assembled monolayer   |
| sat.                   | Saturated  |
| SCE                    | Saturated calomel electrode  |

|                         |   |
|-------------------------|---|
| Sdh(A-D)                | Succinate dehydrogenase subunit   |
| SQ                      | Semiquinone   |
| t                       | Triplet (NMR)   |
| T                       | Absolute temperature [K]  |
| <i>t</i> -BuOK          | Potassium <i>tert</i> -butoxide   |
| THF                     | Tetrahydrofuran   |
| TLC                     | Thin layer chromatography   |
| TMAO                    | Trimethylamine <i>N</i> -oxide  |
| Tris                    | 2-Amino-2-(hydroxymethyl)propane-1,3-diol   |
| <b>U</b> <sub>0-3</sub> | Ubiquinone-terminated OPV-based molecular wire; number indicates length of OPV system |
| UQ/UQH <sub>2</sub>     | Ubiquinone/ubiquinol  |
| <b>U</b> <sub>sat</sub> | Ubiquinone-terminated decanethiol   |
| UV-Vis                  | Ultraviolet–visible (spectroscopy)  |
| <i>v</i>                | Scan rate [V/s]   |
| <i>v</i> <sub>a</sub>   | Anodic critical scan rate [V/s]   |
| <i>v</i> <sub>c</sub>   | Cathodic critical scan rate [V/s]   |
| WE                      | Working electrode   |