Supplementary Material for

Current Advances in Research of Cytochrome c Oxidase

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This document contains details on the pumping mechanism during the reductive reaction phase of the catalytic cycle. Schematic representation of the electrometric results and the sequence of steps during the O→E transition of the reductive phase are shown in Fig. S1. The data are obtained from the electrometric measurements (Belevich et al. 2007) and also derived from the DFT/continuum electrostatic study (Popovic and Stuchebrukhov 2012).
Fig. S1  Schematic representation of the electrometric results and the sequence of steps during the O→E transition of the reductive reaction phase. The numbers correspond to the order of the kinetic phases observed in the experiment (Belevich et al. 2007). The BNC is OH$^-$ ligand of the binuclear catalytic center; the PLS is the proton-loading site of the pump, presumably H291. The donor of the pumped protons – E242 is shown in the two conformations, down and up, as discussed in the review. For the O→E transition, the third phase apparently corresponds to the transfer of a chemical proton along the K-channel; in other transitions, the same proton transfer may take place along the D-channel.
The experimental data for the O→E transition (Belevich et al. 2007) can be interpreted to suggest a mechanism in which the translocation of the pumped proton occurs upon reduction of heme $a$ (Brändén et al. 2005), i.e. before the ET to the BNC, contrary to the proposed model. In contrast, the study on the F→O transition, however, supports the transfer of the pumped proton to PLS upon ET to the binuclear center (Siletsky et al. 2004). These different results may suggest that the oxidative and reductive halves of the catalytic cycle are not entirely identical in all mechanistic details, besides the obvious difference in oxygen chemistry, the redox potentials of metal centers and reaction kinetic rates. It should be noted that the scheme in Fig. 4 (main text) is entirely suitable for the oxidative phase of the catalytic cycle, and in a somewhat modified form (Fig. S1, in Supplementary Material) for the reductive part, as well. Namely, in the reductive phase of the cycle, the steps 2 and 3 are coupled and occur simultaneously. Also step 5, the transfer of a proton to OH$^-$ ligand in the BNC, is accompanied with the complete transfer of an electron to the Cu$_B$ center.

References