Supporting Information

Amdursky et al. 10.1073/pnas.1319351111

SI Discussion

Electrode–Fe Ion vs. Electrode–Heme Edge Separation Distance. Recently, we showed that the conjugated porphyrin ring is the main electron mediator in cytochrome *c* (CytC) (1, 2). Accordingly, one might argue that the separation distance between the electrodes should be considered as a sum of bottom electrode–lower heme edge and top electrode–upper heme edge (Table S1).

As is the case for the current magnitude vs. separation distance plot that was obtained by using the distances to the Fe ion (Fig. 2), also by using the heme edges for the separation distance, there is no linear correlation between the current magnitude and the separation distance (Fig. S4).

Distinguishing Electron Transfer from Electron Transport. Differences between electron transfer (ET) within and electron transport (Etp) across organic molecules have been explored previously. A theoretical study (3) showed that, whereas ET proceeds between two vibronic sinks and can be described by Marcus theory, ETp is a charge-transfer process between two electrodes (thermal baths) and is better described within Landauer theory. At the same time, however, it was found theoretically (4, 5) and confirmed for some systems experimentally (6, 7) that ET and ETp can be related either linearly (6) or, more generally, by a power law (7). Thus, the clear difference between ETp and ET in terms of distance–efficiency correlation may have its cause in these basic differences between the two processes.

1. Amdursky N, Pecht I, Sheves M, Cahen D (2013) Electron transport via cytochrome c on Si-H surfaces: Roles of Fe and heme. *J Am Chem Soc* 135(16):6300–6306.
2. Amdursky N, Ferber D, Pecht I, Sheves M, Cahen D (2013) Redox activity distinguishes solid-state electron transport from solution-based electron transfer in a natural and artificial protein: Cytochrome C and hemin-doped human serum albumin. *Phys Chem Chem Phys* 15(40):17142–17149.
3. Nitzan A, Ratner MA (2003) Electron transport in molecular wire junctions. *Science* 300(5624):1384–1389.
4. Nitzan A (2001) A relationship between electron-transfer rates and molecular conduction. *J Phys Chem A* 105(12):2677–2679.
5. Nitzan A (2002) The relationship between electron transfer rate and molecular conduction. 2. The sequential hopping case. *Isr J Chem* 42(2–3):163–166.
6. Adams DM, et al. (2003) Charge transfer on the nanoscale: Current status. *J Phys Chem B* 107(28):6668–6697.
7. Wierzbinski E, et al. (2013) The single-molecule conductance and electrochemical electron-transfer rate are related by a power law. *ACS Nano* 7(6):5391–5401.

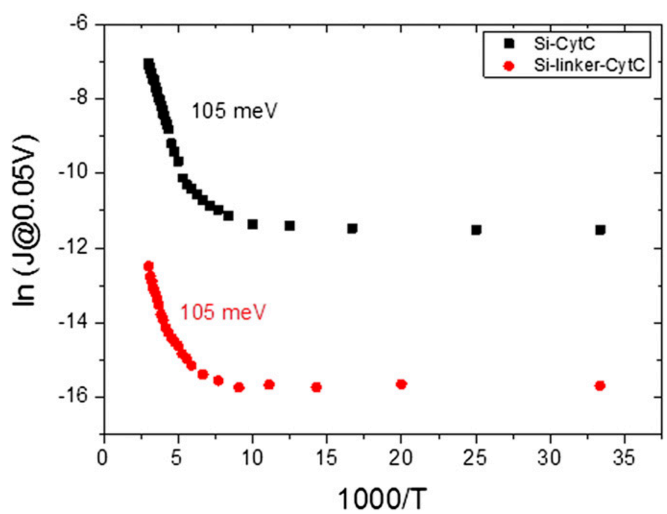

Fig. S1. Current density (J; measured at 0.05 V, plotted on an ln scale) as a function of inverse temperature (T) for WT CytC, bound via a carboxylate-terminated linker to SiO_x/Si (red circles; as displayed in Fig. 1) and WT CytC, electrostatically absorbed directly onto Si–H surfaces (black squares; modified from ref. 1).

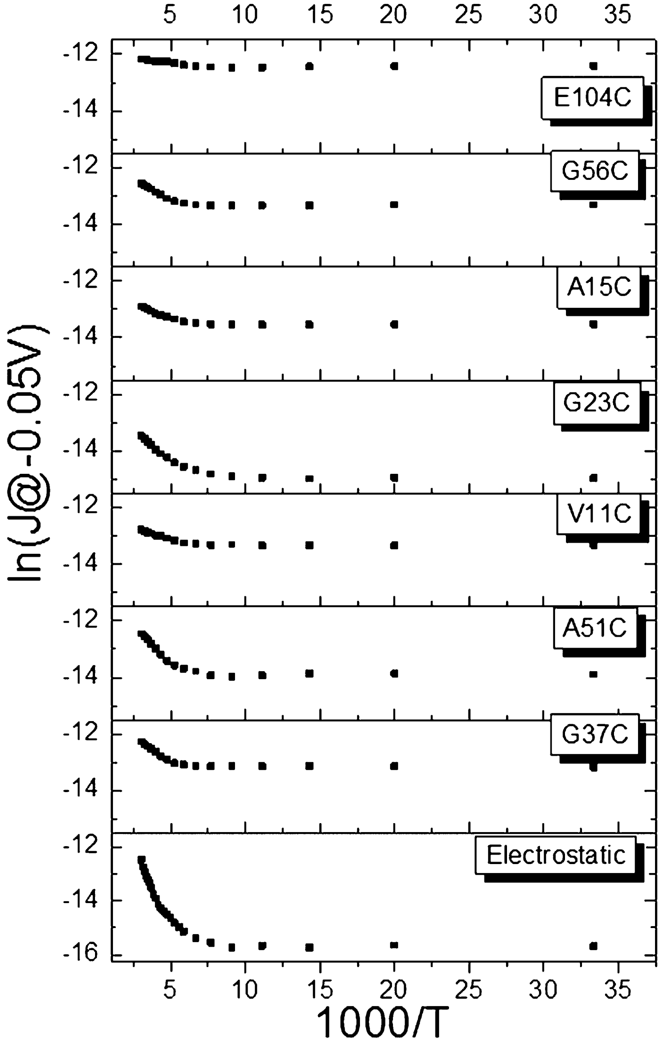

Fig. S2. Current density (measured at 0.05 V, plotted on an ln scale) as a function of inverse temperature of all of the seven different covalently bound CytC mutants and of the electrostatically bound WT CytC.

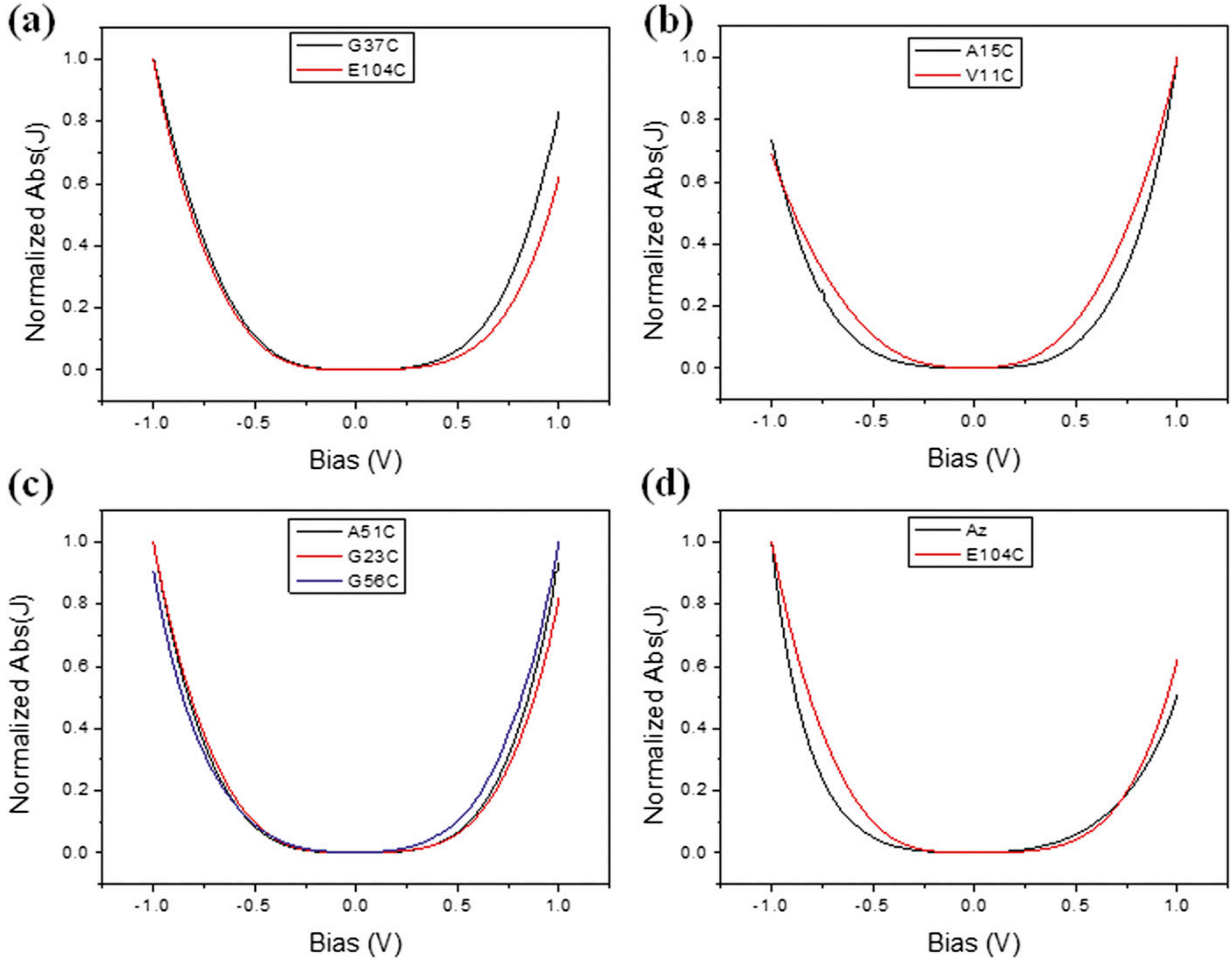

Fig. S3. Normalized current–voltage of the various CytC mutants used in this study: (*A*) G37C and E104C, (*B*) A15C and V11C, (*C*) A51C, G23C, and G56C, and (*D*) a comparison between the E104C CytC mutant and WT azurin (Az).

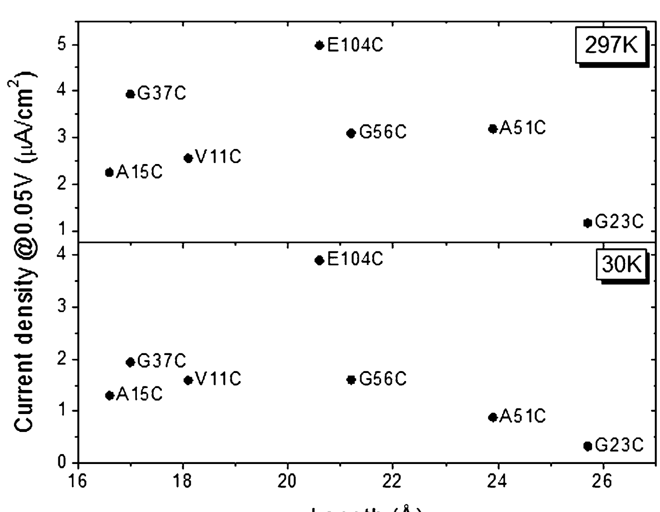

Fig. S4. Current density (measured at 0.05 V) as a function of the length of the protein (the sum of the bottom electrode–lower heme edge and upper heme edge–top electrode distances) at room temperature and 30 K (*Upper* and *Lower*, respectively).

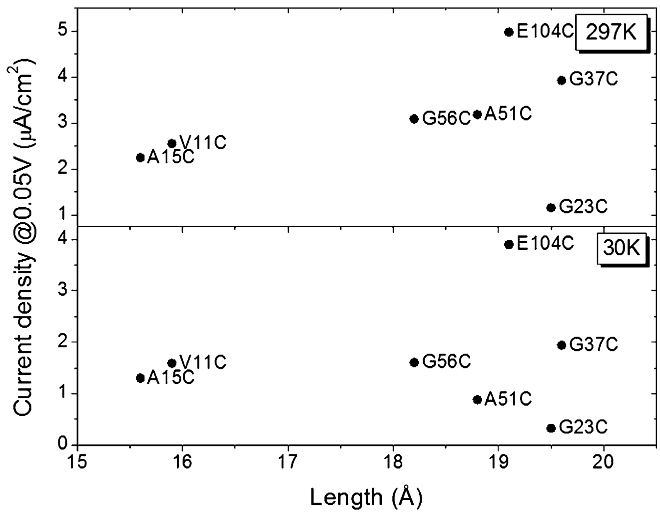

Fig. S5. Current density (measured at 0.05 V) as a function of the longest distance between the bottom electrode and the Fe ion or the Fe ion and the top electrode at room temperature and 30 K (*Upper* and *Lower*, respectively).

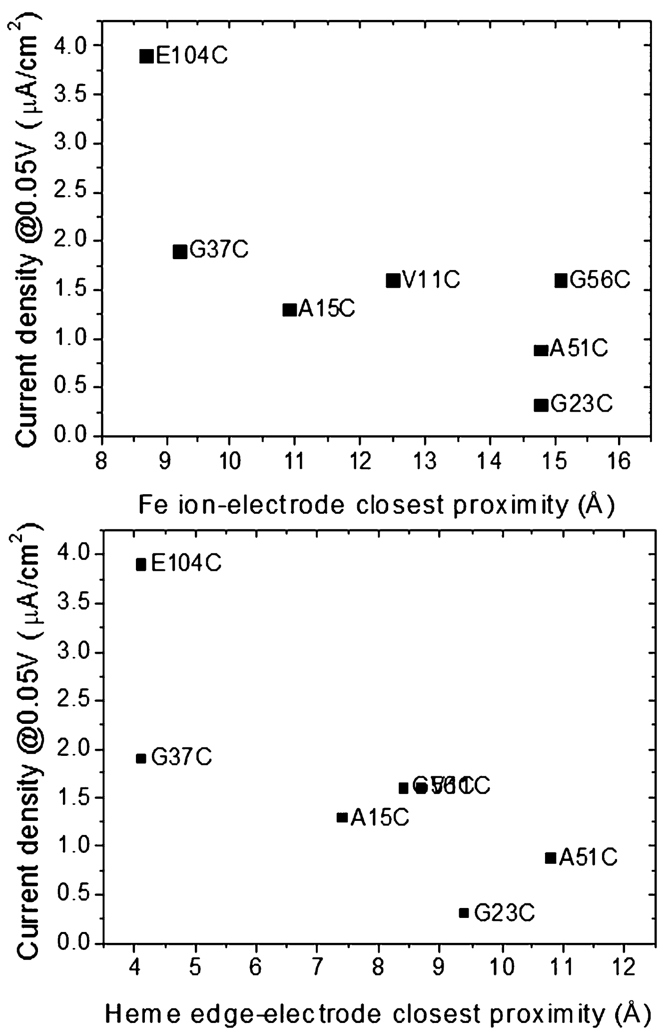

Fig. S6. Current density (measured at 0.05 V) as a function of the closest Fe ion–electrode proximity (the distance between the heme and the top or bottom electrode, whichever is closest, taken at 30 K; *Upper*) and the heme edge–electrode closest proximity (*Lower*). The overlapping entries in the lower part of the figure are those of V11C and G56C.

Table S1. Shortest heme edge–electrode distances

Mutant	Distance Cys–lower heme edge, ±0.1 Å*	Distance upper heme edge–top electrode, Å*	Sum of distances, Å*	Heme ring angle with the plane of the substrate*, °
A51C	10.8	13.1 (1.8)	23.9	155
G23C	16.3	9.4 (1.0)	25.7	170
G56C	12.8	8.4 (2.1)	21.2	95
A15C	7.4	9.2 (0.6)	16.6	109
G37C	12.9	4.1 (0.1)	17	91
V11C	9.4	8.7 (0.7)	18.1	77
E104C	16.5	4.1 (0.2)	20.6	115

*We used those amino acids that are most likely contacting the top electrode, calculated the distances with each of these, and averaged. The SDs appear in parentheses.