Supporting Information

Amdursky et al. 10.1073/pnas.1210457110

SI Text

Thermally Activated vs. Temperature-Independent ETp in Az. Thermally activated electron transport (ETp) via the deuterated azurin (Az) at ≥180 K (Fig. 3*B*, black squares) can be fitted to an Arrhenius equation [$\propto \exp(-E_a/k_BT)$], with $E_a = 85$ meV (8.2 kJ/mol). As shown previously (1), >∼180 K ETp via protium-Az becomes thermally activated upon Cu ion removal (yielding apo-Az) with $E_a = 320$ meV (33 kJ/mol). Although E_a for ETp via deuterated Az is much lower than via apo-Az, the change to thermal activation is remarkable, because the deuterated protein still contains the Cu redox center.

A possible explanation for how deuteration can change ETp >180 K to temperature dependent is based on the fact that activationless ET may be observed if the potential energy curve of the acceptor crosses that of the donor at the latter's minimum energy. Then the reorganization energy of the process, λ, equals the ET driving force, $-\Delta G^0$, and the k_{ET} is maximal (2). In such a case even a minor shift of the nuclear potential curves by the H/D exchange (3) will move the crossing point and lead to a thermally activated barrier for transport, as observed in our measurements.

1. Sepunaru L, Pecht I, Sheves M, Cahen D (2011) Solid-state electron transport across azurin: From a temperature-independent to a temperature-activated mechanism. *J Am Chem Soc* 133(8):2421–2423.
2. Marcus RA, Sutin N (1985) Electron transfers in chemistry and biology. *Biochim Biophys Acta* 811(3):265–322.
3. Kavner A, Bonet F, Shahar A, Simon J, Young E (2005) The isotopic effects of electron transfer: An explanation for Fe isotope fractionation in nature. *Geochim Cosmochim Acta* 69(12):2971–2979.

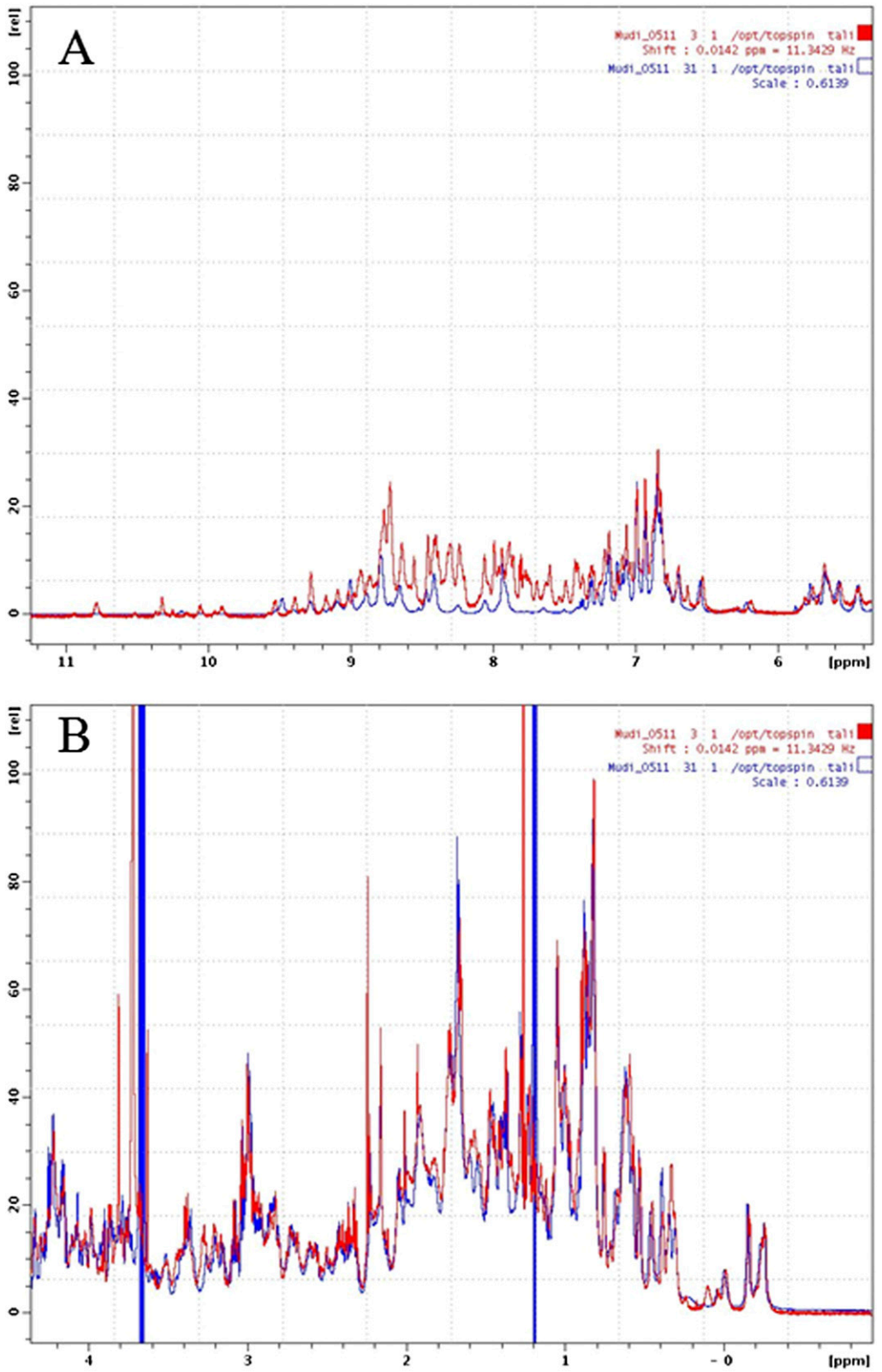

Fig. S1. Superposition of 1D 1H NMR spectra of protium- and deuterium-labeled Az (red and blue curves, respectively). (*A*) Aromatic and amide region of the spectrum, showing signals of aromatic and exchangeable amide protons. (*B*) Aliphatic region of the spectrum, showing signals of nonexchangeable protons.

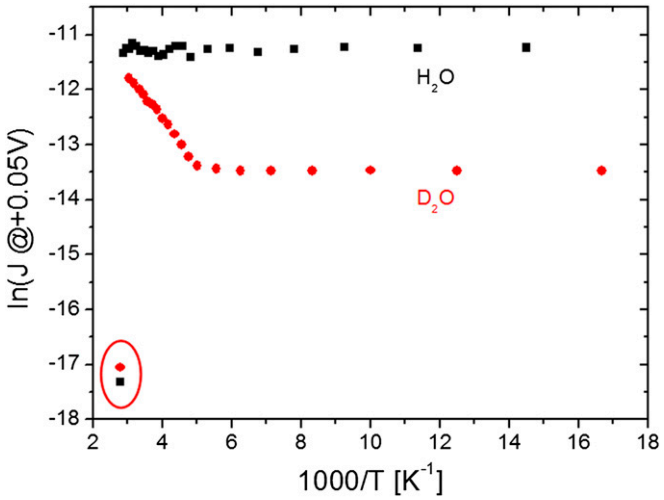

Fig. S2. Current density at −50 mV vs. inverse temperature of protium- and deuterium-labeled Az with an Au pad as top contact (i.e., by lift-off, float-on technique). The red circle indicates the denaturation point of the protein.