Supporting Materials for:
Glassy protein dynamics and gigantic solvent reorganization energy of plastocyanin

David N. LeBard and Dmitry V. Matyushov
Center for Biological Physics, Arizona State University, PO Box 871604, Tempe, AZ 85287-1604

Figure S1 shows the Cu-O distribution function calculated for Ox and Red states of PC at 285 and 310 K. Figure S2 shows the vibrational density of states of plastocyanin (PC) calculated from quasi-harmonic analysis implemented in Amber8.0. The peak of the density of vibrational states at about 36 cm^{-1} is in agreement with the low-frequency vibrations with ca. 33 cm^{-1} seen in Raman spectra of plastocyanin.[1]

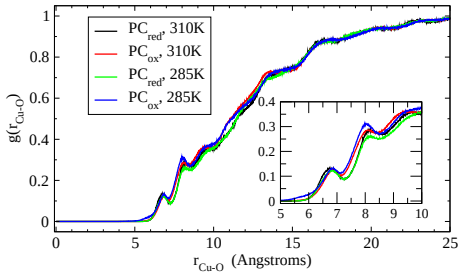

FIG. S1: Radial distribution function between plastocyanin's copper atom and the water's oxygen.

Figure S3 presents an example of Stokes shift correlation functions calculated from 400 ps and a 10 ns windows. The Stokes shift functions are fitted to eq (14) to extract the fast and slow relaxation components. The hundreds of picoseconds tail seen in the 10 ns average is completely lost for the narrow time window. The value for β also changes from $\beta = 0.69$ characteristic of heterogeneous dynamics to $\beta = 1$ of the exponential decay when the observation window is narrowed.

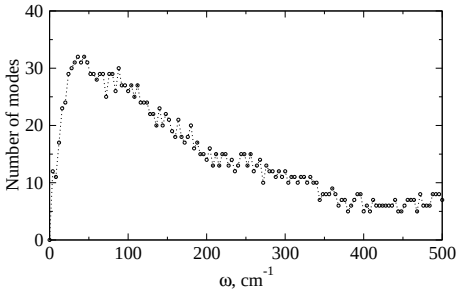

FIG. S2: Vibrational density of states of plastocyanin in TIP3P water at 310 K.

[1] Nakashima, S.; Nagasawa, Y.; Seike, K.; Okada, T.; Sato, M.; Kohzuma, T. *Chem. Phys. Lett.* **2000,** *331,* 396.
[2] Duan, Y.; Wu, C.; Chowdhury, S.; Lee, M. C.; Xiong, G.; Zhang, W.; Yang, R.; Cieplak, P.; Luo, R.; Lee, T.; Caldwell, J.; Wang, J.; Kollman, P. *J. Comp. Chem.* **2003,** *24,* 1999-2012.
[3] Ullmann, G. M.; Knapp, E.-W.; Kostić, N. M. *J. Am. Chem. Soc.* **1997,** *119,* 42-52.
[4] Solomon, E.; Szilagyi, R.; DeBeerGeorge, S.; Basumallick, L. *Chem. Rev.* **2004,** *104,* 419-458.
[5] Kerpel, J. O. D.; Ryde, U. *Proteins: Structure, Function, and Genetics* **1999,** *36,* 157-174.

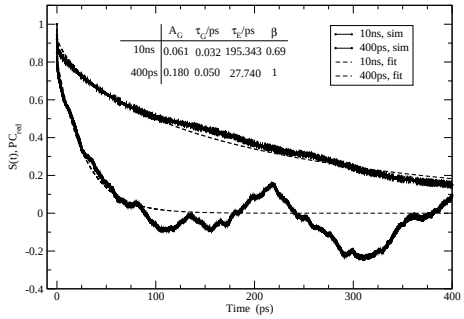

FIG. S3: Stokes shift correlation function for reduced state at 310 K using a 400 ps and 10 ns windows. The dashed lines are fits to eq (14) with the fitting parameters displayed in the plot.

TABLE S1: Charging scheme of plastocyanin for MD simulations. The Δz_j charge differences refer to the change from red to ox.

Scheme	$N_{\Delta z}$	Δz_j atom (Res. Number)	$\Delta z_j/e$	Params: Protein, ligands
$Q1$	1	Cu	1.0	AmberFF03[2]
	4	Cu	0.840	AmberFF03[2], Charmm22/Expt.[3,4]
$Q2$		$S_\gamma(84)$	0.109	
		$N_\delta(37)$	0.025	
		$N_\delta(87)$	0.025	
	33	Cu	0.134	AmberFF03[2], DFT[5]
		$C_\beta(37)$	0.050	
		$C_\gamma(37)$	−0.156	
		$N_{\delta1}(37)$	0.110	
		$C_{\epsilon1}(37)$	−0.049	
		$H_{\epsilon1}(37)$	0.027	
		$N_{\epsilon2}(37)$	−0.003	
		$H_{\epsilon2}(37)$	0.045	
		$C_{\delta2}(37)$	0.081	
		$H_{\delta2}(37)$	0.037	
		$C_\alpha(84)$	−0.064	
		$C_\beta(84)$	0.337	
		$H_{\beta3}(84)$	−0.039	
		$H_{\alpha2}(84)$	−0.039	
		$S_\gamma(84)$	0.339	
		$C_\beta(87)$	−0.007	
$Q3$		$C_\gamma(87)$	−0.005	
		$N_{\delta1}(87)$	0.009	
		$C_{\epsilon1}(87)$	0.030	
		$H_{\epsilon1}(87)$	−0.003	
		$N_{\epsilon2}(87)$	0.002	
		$H_{\epsilon2}(87)$	0.038	
		$C_{\delta2}(87)$	0.035	
		$H_{\delta2}(87)$	0.046	
		$C_\beta(92)$	−0.033	
		$C_\gamma(92)$	0.216	
		$H_{\gamma2}(92)$	−0.056	
		$H_{\gamma3}(92)$	−0.056	
		$S_\delta(92)$	−0.094	
		$C_\epsilon(92)$	0.224	
		$H_{\epsilon1}(92)$	−0.052	
		$H_{\epsilon2}(92)$	−0.052	
		$H_{\epsilon3}(92)$	−0.052	