

Supplementary Information

RESULTS - extension

Measurements in the presence of o-phenanthroline. The kinetic origins of the slowed overall recombination at low temperature were confirmed through equivalent measurements performed on RCs in the presence of the Q_B-site inhibitor o-phenanthroline, which is known to slow down the rate of $P^+H_A^- \rightarrow PH_A$ recombination.^{3,13} Lifetimes and amplitudes obtained from an analysis of the experimental data are collected in Table 1 in the main text. As shown in Figure S1A,B the temperature dependences of the lifetimes and amplitudes associated with decay of H_A^- were qualitatively very similar to those obtained for RCs without o-phenanthroline (see main text). Comparative analysis of these two preparations indicated that the addition of o-phenanthroline generally slowed charge recombination mostly by changing the relative amplitudes of particular components: at all temperatures the amplitude of the fastest phase (A_1) decreased and that of the constant (A_4) increased after addition of o-phenanthroline (Figure S1B compared with Figure 3B in main text). The effect of o-phenanthroline on the amplitudes of the two remaining components, A_2 and A_3 , could not be judged unambiguously (see below). The observed general effect of o-phenanthroline of slowing overall charge recombination across the range of temperatures was consistent with the previous reports on its effect at room temperature.^{3,13}

Dependence of kinetics on temperature above and below 200 K. In general the middle and slow lifetimes showed the greatest dependence on temperature above 200 K, but reached a maximal value below this temperature (Figure S1A and Figure 3A in the main text, and see also Figure 1 in the main text). This was particularly clear in the case of RCs with o-phenanthroline (Figure S1A) and the τ_2 component for RCs without o-phenanthroline (main text, Figure 3A, red/circles). In the case of the slow τ_3 component for the RCs without o-

phenanthroline (main text Figure 3A, green/up-triangles) the saturation character of the dependence was less certain, but this may have been due to some uncertainty in the fits between the middle and slow components (main text, Figures 3A and B). This arose because of the limited signal to noise ratio of the experimental data, free fits tending to over- or underestimate the lifetimes and, in compensatory way, under- or overestimate the respective amplitudes of the two components. As can be seen in Figure 3A of the main text, at 77 K the lifetime τ_3 “protruded” towards a high value and at 150 K τ_3 “protruded” towards a low value relative to the expected plateau level of the order of ~ 35 ns (green/up-triangles in Figure 3A of the main text; compare to green/up-triangles in Figure S1A). The larger value of τ_3 at 77 K (main text, Figure 3A, green/up-triangles) was compensated by a smaller amplitude A_3 at this temperature (main text, Figure 3B, green/up-triangles), and an opposite effect was seen at 150 K. This variance of the A_3 amplitude in the region from 77 to 200 K was further compensated by a similar but “opposite in phase” variance of the amplitude of the middle component (A_2) (main text, Figure 3B, green/up-triangles and red/circles, respectively).

DISCUSSION - extension

Simulations with artificially increased amplitudes D_1 . Due to the limited temporal resolution of the nanosecond measurements the corrected amplitudes D_1 are certainly underestimated. Therefore, we performed additional simulations with artificially increased amplitudes D_1 up to ~ 0.4 and ~ 0.2 at room and liquid nitrogen temperatures, respectively and keeping the ratios between the remaining amplitudes D_2 - D_4 unchanged. This had a moderate influence on the parameters derived from the calculations. The most notable conclusions naturally concern the branching between indirect charge recombination and relaxation of the state $(P^+H_A^-)_1$ and comprise: 1) an increase of τ_{12} to 1.0 ± 0.1 ns at all temperatures and 2) a

decrease of τ_{PB} from 1.1 to ~ 0.6 ns at all temperatures. The remaining conclusions were essentially unchanged.

Uncertainty of τ_{PB} and ΔG_i .

The exact value of the parameter τ_{PB} is not known and difficult to determine. On the other hand, τ_{PB} and ΔG_2 (or ΔG_3) are two compensating parameters in fitting the curves in Fig. 5B-C of the main text. Consequently, changing τ_{PB} between 0.07 and 0.6 ns influences the values of ΔG_2 (which changes from 120 to 70 meV, respectively) and ΔG_3 (which changes from 160 to 110 meV, respectively) without dramatic change in the fits quality, and has no impact on the major conclusions drawn in this paper. Naturally, the amplitudes of the two phases of relaxation but not the lifetimes, shown in Figure 6 of the main text, would be affected by changing τ_{PB} and ΔG_i .

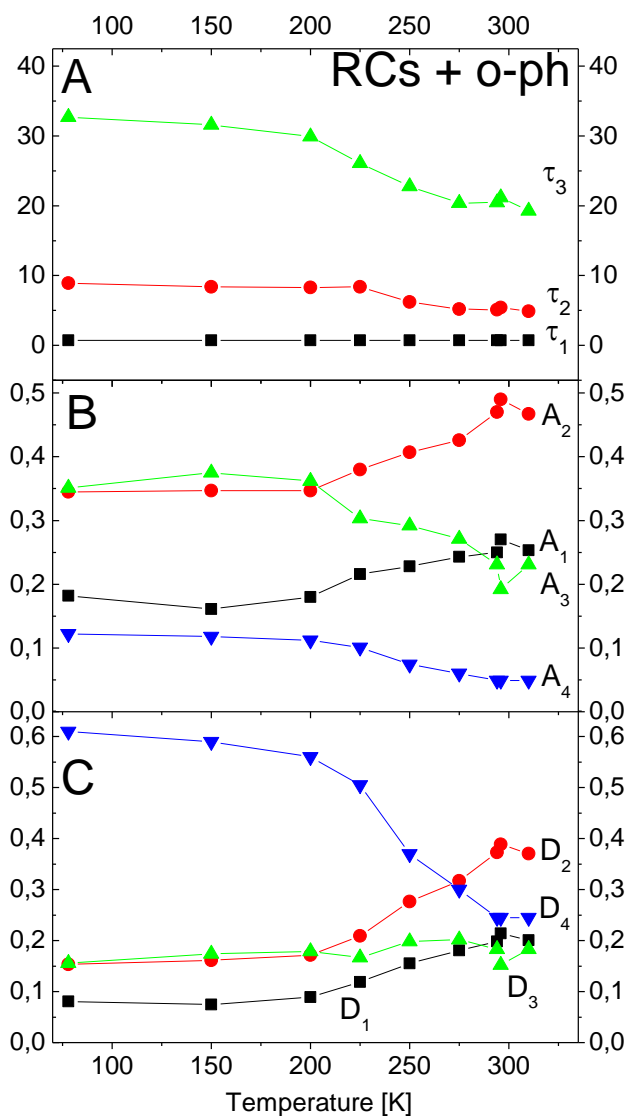


Figure S1. Temperature-dependence of parameters from analysis of absorption changes at 690 nm for RCs with o-phenanthroline (A, B). The kinetic scheme (Eq. 1, main text) comprised three exponential decays and a constant component, producing three lifetimes (A) and four amplitudes (B). Panel C presents amplitudes that have been corrected as described in the main text.