Biological Relevance of Charge Transfer Branching Pathways in Photolyases

Supporting Information

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Electronic coupling between the Tryptophans

The electronic couplings correspond to the off-diagonal elements of the coarse-grained Hamiltonian detailed in the main manuscript. We reported in Table S1 the electronic couplings between close tryptophans in the branching pathway.

Table S1: Electronic couplings between the different tryptophans fragments along the branching pathway during the 150 ns classical MD.

	Couplings / meV
A-B1	15.7 ±9.2
B1-C1	4.3 ±5.2
A-B2	5.1 ±3.9
B2-C2	10.7 ± 0.1
C2-D2	11.0 ± 0.1

Details of the charge transfer simulations

We selected one simulation of the charge propagation along the branched pathways to illustrate the three steps mechanism of the charge transfer in PhrA. In the movie phra.mpg, the residues are colored according to their occupation: red is 0, blue is 1 and green is 0.5. In this simulation, the positive charge first goes from **A** to **C1** in few ps (high occupation value) and then its fluctuates between **B1** and **C1**. After 300 ps, the charge is transferred on the alternative tetrad and fixed on **D2** after 400 ps. Figure S1 shows the occupation of the different tryptophans along the trajectory.

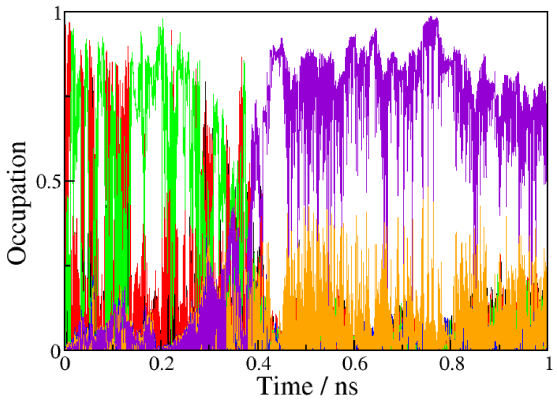

Figure S1: Occupation of the different tryptophans during the selected simulation of the charge propagation along the two pathways. **A**, black; **B1**, red; **C1**, green; **B2**, blue; **C2**, orange; **D2**, purple.

In the simulation and especially during the crossing between both pathways, the charge can be delocalized over several residues during some decades of picoseconds. In the movie,

this situation corresponds to the frames where several residues are green. This delocalization is probably an artifact due to our propagation scheme. However, most of the time, the charge is mainly localized on **C1** or **D2** as underlined by the occupation distribution given in Figure S2. All sites present a high probability to have between 0 and 20% of the charge but only **C1** and **D2** have a significant probability to accept around 80-90% of the positive charge.

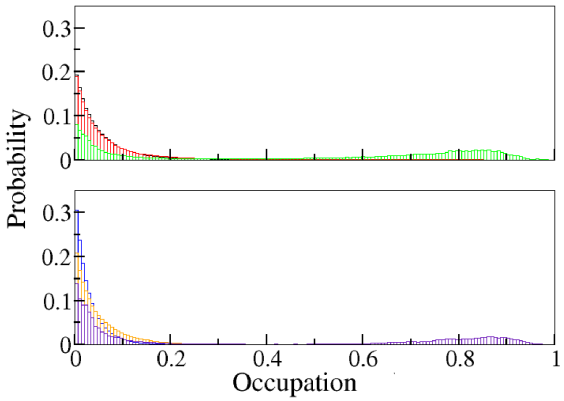

Figure S2: Histogram of the occupation density for all Trp in the 29 QM/MM simulations including both pathways in the QM part. Black line: **A**; red line: **B1**; green line: **C1**; blue line: **B2**; orange line: **C2**; purple line: **D2**