Stabilization of Charge-Transfer States in Photosystem II Reaction Centers: Insights From Multiscale Modeling

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The initial kinetic processes of oxygenetic photosynthesis occur in photosystem II where bound excitons are transported to the reaction centers and then separated into free-carriers. Experimental observations find that the charge-separation occur with near-unity yield, but the mechanisms are yet to be clearly delineated. Here we use multiscale QM/MM approaches combined with time-dependent density functional theory to explore the (non)-equilibrium charge-transfer excited-states of the 'special-pair' P_{D1} - P_{D2} dimer in the photosystem II reaction center. We find that the non-equilibrium CT excited-state resides near the Soret band making the exciton the lowest-energy excited-state. When including equilibration of nuclear and dielectric degrees of freedom along the charge-transfer potential energy surface the charge-transfer state becomes energetically stabilized below the excitonic state. This work indicates that charge-separation can occur at the 'special-pair' at time-scales beyond sensitization to provide a kinetic pathway for promoting photosynthesis.