A highly energetic charge-separated state and factors governing its light-induced formation and decay

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Charge-separated states are key intermediates in photosynthesis-inspired multielectron transfer reactions in photosynthesis.[1] However, the factors that govern the formation efficiencies of charge-separated states are still poorly understood.[2] Moreover, light-induced electron-hole recombinations as main deactivation pathways, which are largely unexplored, compete with the desired charge accumulations.[3] We present a systematic investigation[4] of two donor-photosensitizer-acceptor triads[5] capable of storing as much as 2.0 eV in their charge-separated states The triads have different donor-acceptor distances allowing us to include distance-dependence investigations. Our study provides deep insights into the charge-separated state formation quantum yields, which can reach up to 80%, using quantitative one-pulse laser flash photolysis. Additional two-pulse laser flash photolysis experiments[6] elucidate the fate of the charge-separated state upon further (secondary) excitation with green photons. One key finding of our study is that light-induced and thermal charge recombinations (Figure 1) show opposite behaviors in terms of their distance dependences.

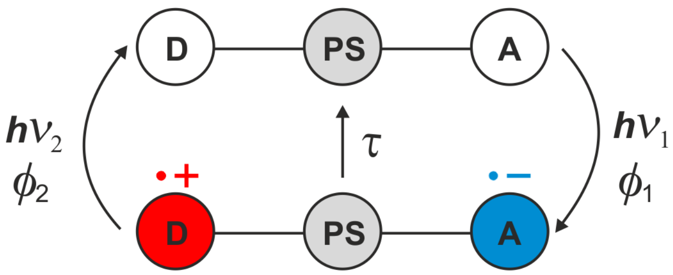

Figure 1: Schematic representation of the mechanism for light-induced ($h\nu_1$) formation of a charge-separated state in a molecular electron donor-photosensitizer-electron acceptor triad together with thermal (τ) and light-induced ($h\nu_2$) charge recombination.

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