Supporting information

Figure S1: Pump-rePump-Probe kinetics of peridinin in methanol. Peridinin was excited at 400-nm, and then repumped, at a delay of 1 ps, by pulses of 620-nm. (A) Pump-Probe (blue), Pump-rePump-Probe (red) and (B) $\Delta \Delta OD$ (black) kinetic traces measured at 610 nm, close to the peak of the ICT absorption. The repump pulse induces an instantaneous loss of excited state absorption signal by moving population from the ICT state to a higher excited stateand subsequently the signal recovers fully within a few picoseconds. The inset zooms on the repump. (C): Pump-Probe (blue) and Pump-rePump-Probe (red) and (D) $\Delta \Delta OD$ (black) spectra measured at 740 nm, where the signal is positive at early times due to the excited state absorption of S₂ and then negative due to the stimulated emission of the ICT state. Upon repumping, we observe an instantaneous loss of stimulated emission as population is removed from the ICT state. The signal becomes positive for a short time, manifesting the transient population finds its way to the ICT state and that no additional species is populated, unlike when an 800-nm pulse is used.

Figure S2: A comparison between the pump-probe spectra (blue lines) and the $\Delta\Delta$ OD spectra (black lines) measured after excitation of peridinin in methanol at 400 nm and dumping at 3 ps with 800-nm pulses. All spectra have been normalized at the peak of the excited state absorption and the $\Delta\Delta$ OD spectra have been inverted, to facilitate the comparison of their shapes. A: the PP and $\Delta\Delta$ OD spectra measured 0.5 ps after the dump, B: the PP and $\Delta\Delta$ OD spectra measured 11 ps after the dump.



Papagiannakis et al, Fig S1

