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Supporting Information

Coordination of the Biliverdin D-ring in Bacteriophytochromes

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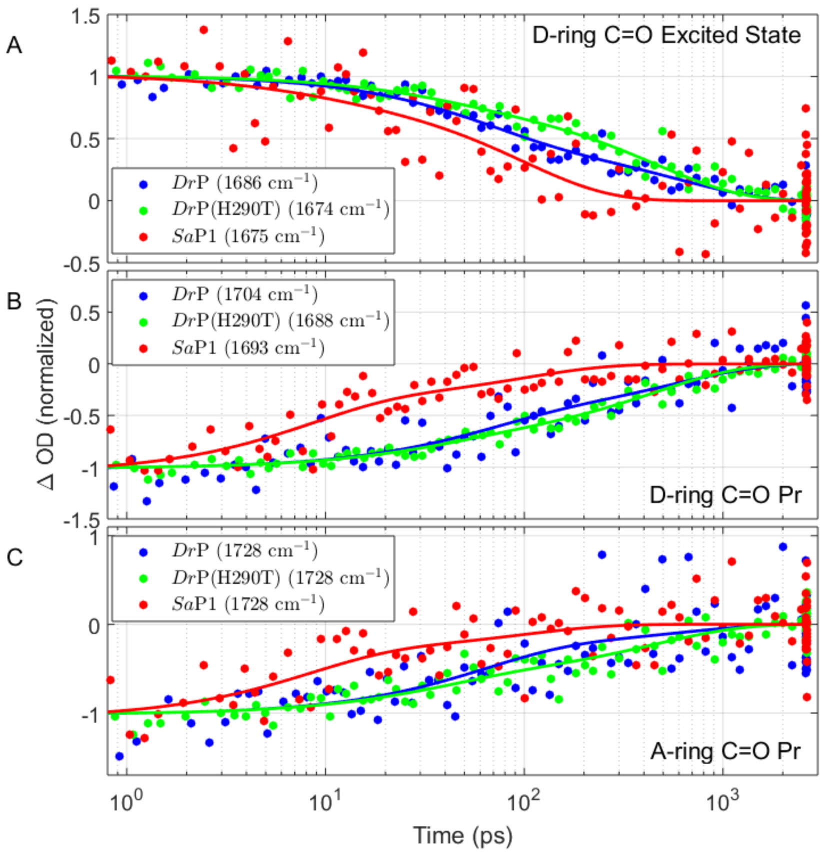

Figure SI 1, Normalized time traces of the IR signals of the carbonyl groups of the biliverdin at the excited state absorption of the D-ring (A), at the bleach of the D-ring (B), and at the bleach of the A-ring (C), of the *Dr*P $_{PSM}$ (blue), *Dr*P(H290T) $_{PSM}$ (green), and *Sa*P1 $_{PSM}$ (red) samples. The lines are the global analysis fits. The data shows that the excited state decay is faster for *Sa*P1 $_{PSM}$ than for *Dr*P $_{PSM}$. On the other hand, *Dr*P(H290T) $_{PSM}$ is slightly slower than *Dr*P $_{PSM}$.

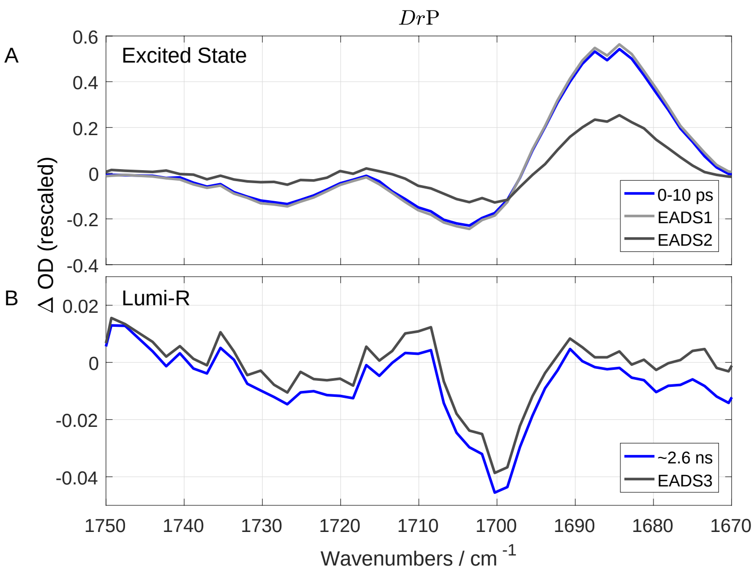

Figure SI 2, Comparison of the Evolution associated difference spectra and the raw spectral data at the early time points (A) and at the late time-points (B) of *Dr*P $_{PSM}$. The 2.6 ns spectral information is obtained by integrating signals from 30 different time-points within a distribution of 5 ps around the 2.6 ns. The detected spectrum at 0-10 ps overlays very well with the EADS and the spectral difference between EADS1 and EADS2 pinpoints the need of introduction of a second time-component to the analysis.

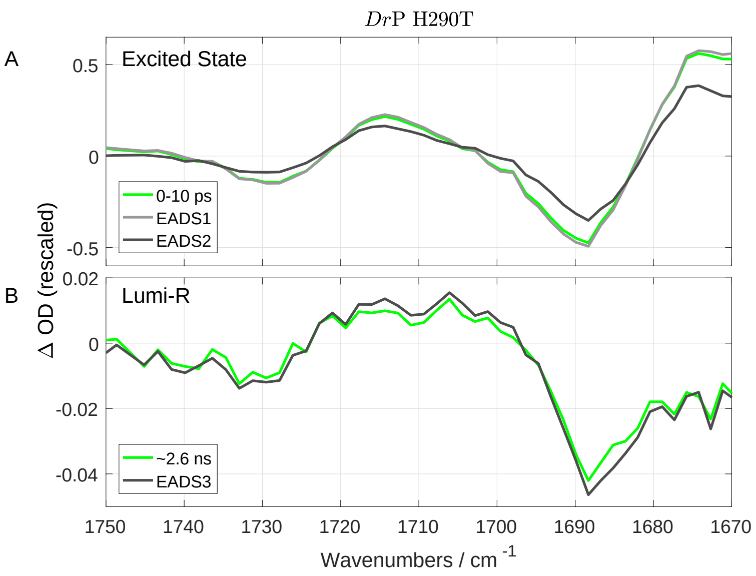

Figure SI 3, Comparison of the Evolution associated difference spectra and the raw spectral data at the early time points (A) and at the late time-points (B) of *Dr*P(H290T) $_{PSM}$. The 2.6 ns spectral information is obtained by integrating signals from 30 different time-points within a distribution of 5 ps around the 2.6 ns. The detected spectrum at 0-10 ps overlays very well with the EADS and the spectral difference between EADS1 and EADS2 pinpoints the need of introduction of a second time-component to the analysis.

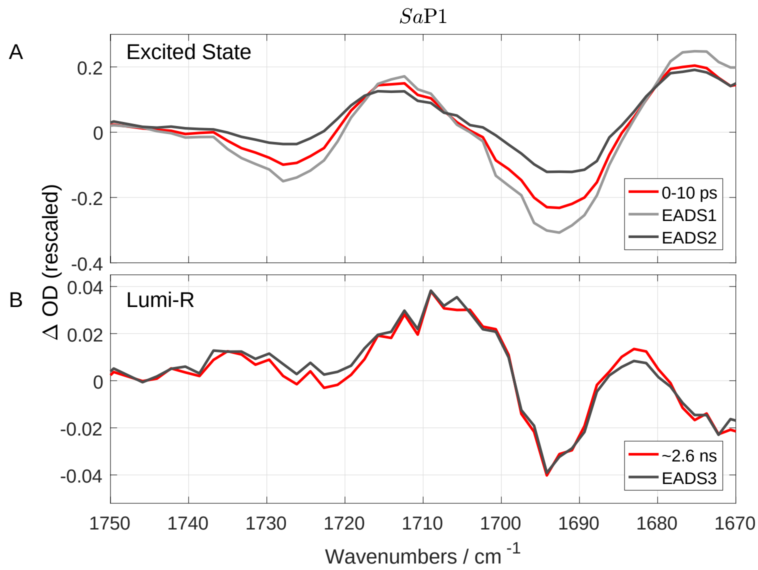

Figure SI 4, Comparison of the Evolution associated difference spectra (EADS) and the raw spectral data at the early time points (A) and at the late time-points (B) of *Sa*P1$_{PSM}$. The 2.6 ns spectral information is obtained by integrating signals from 30 different time-points within a distribution of 5 ps around the 2.6 ns. The spectral shape, detected at 0-10 ps, follows the spectral features of the EADS1. However, as the lifetime of the EADS1 is clearly shorter, the amplitude of the EADS1 is larger.

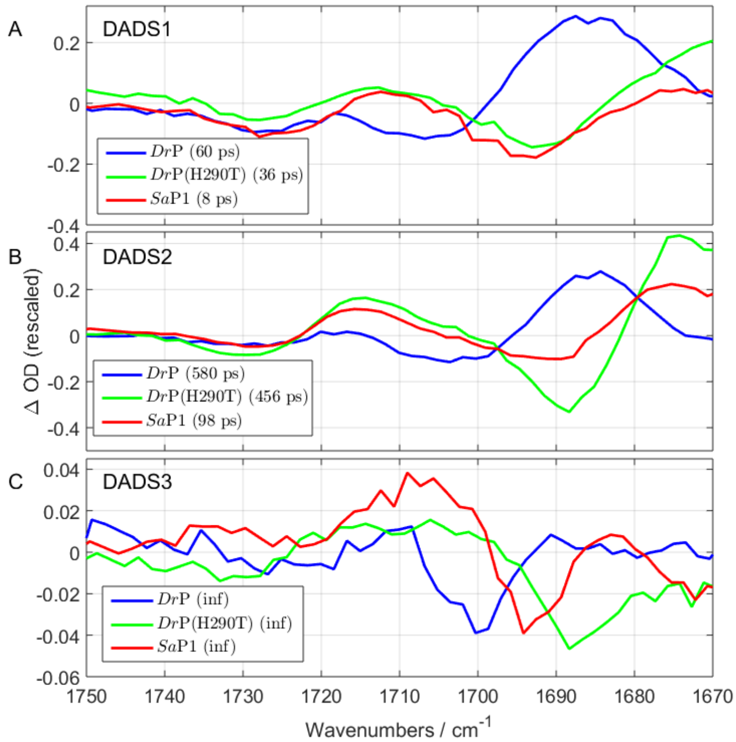

Figure SI 5, Decay-associated difference spectra (DADS) of *Dr*P$_{PSM}$, *Dr*P(H290T)$_{PSM}$, and *Sa*P1$_{PSM}$. The DADS were obtained by the same global analysis as the EADS in Fig. 5. Whereas the EADS assume a sequential model, the DADS are the result of a model with components decaying in parallel. The associated time constants are therefore the same.

Table SI 1, Decay times (τ) and amplitudes of the DADS (A) of three components in the global analysis.

	*Dr*P$_{PSM}$		*Dr*P(H290T)$_{PSM}$		*Sa*P1$_{PSM}$	
Component	τ	A*	τ	A*	τ	A*
1	60 ps	0.57	36 ps	0.30	8 ps	0.41
2	580 ps	0.39	456 ps	0.63	98 ps	0.49
3	non decaying**	0.05	non decaying**	0.07	non decaying**	0.10
τ_{ave}***	260 ps		298 ps		51 ps	

* A was estimated by integrating the DADS over the detected spectral range, the confidence range is 20%.

** The lifetime of the non-decaying component τ_3 was fixed to 100 ns.

*** τ_{ave} is computed as $\tau_1 \cdot A_1 + \tau_2 \cdot A_2$