Supporting Information

Photoisomerization of phytochrome´s chromophore: A vibrational spectroscopic view on the primary ground state processes.

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Resonance Raman spectra of Agp2

RR spectra were measured of Agp2 in the Pfr, Lumi-F, and Pfr´ states as highlighted in the photocycle in Figure S1. In the three states, H/D exchange of the ring D N-H is impaired such that a selected H/D substitution at rings A, B, C vs. ring D is possible.[1,2]

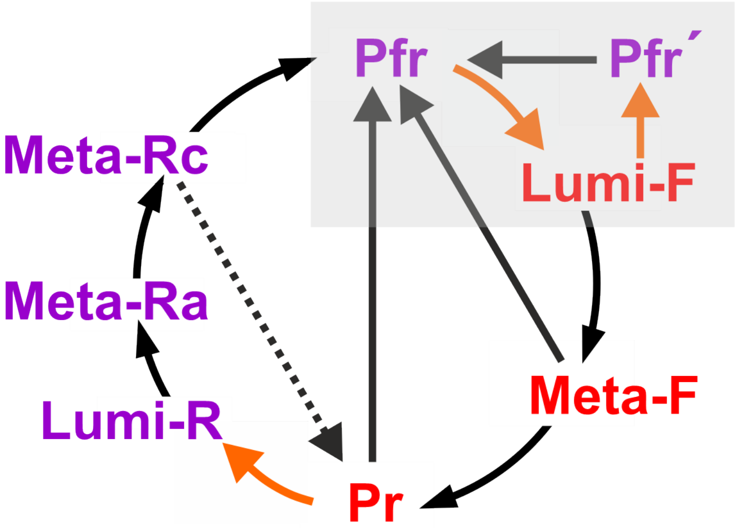

Figure S1. Photocycle of Agp2 and Agp1 with the states in ZZEssa configuration in violet and the states in ZZZssa configuration in red.[3] The orange and black arrows indicate photochemical and black reactions, respectively. The black dotted line represents a reaction that is very likely but not yet confirmed. The gray rectangle highlights those states of Agp2, the RR spectra of which are shown in Figures S2 – S4. The Pfr´ state has been so far only detected for Agp2.

1. RR spectra of Pfr

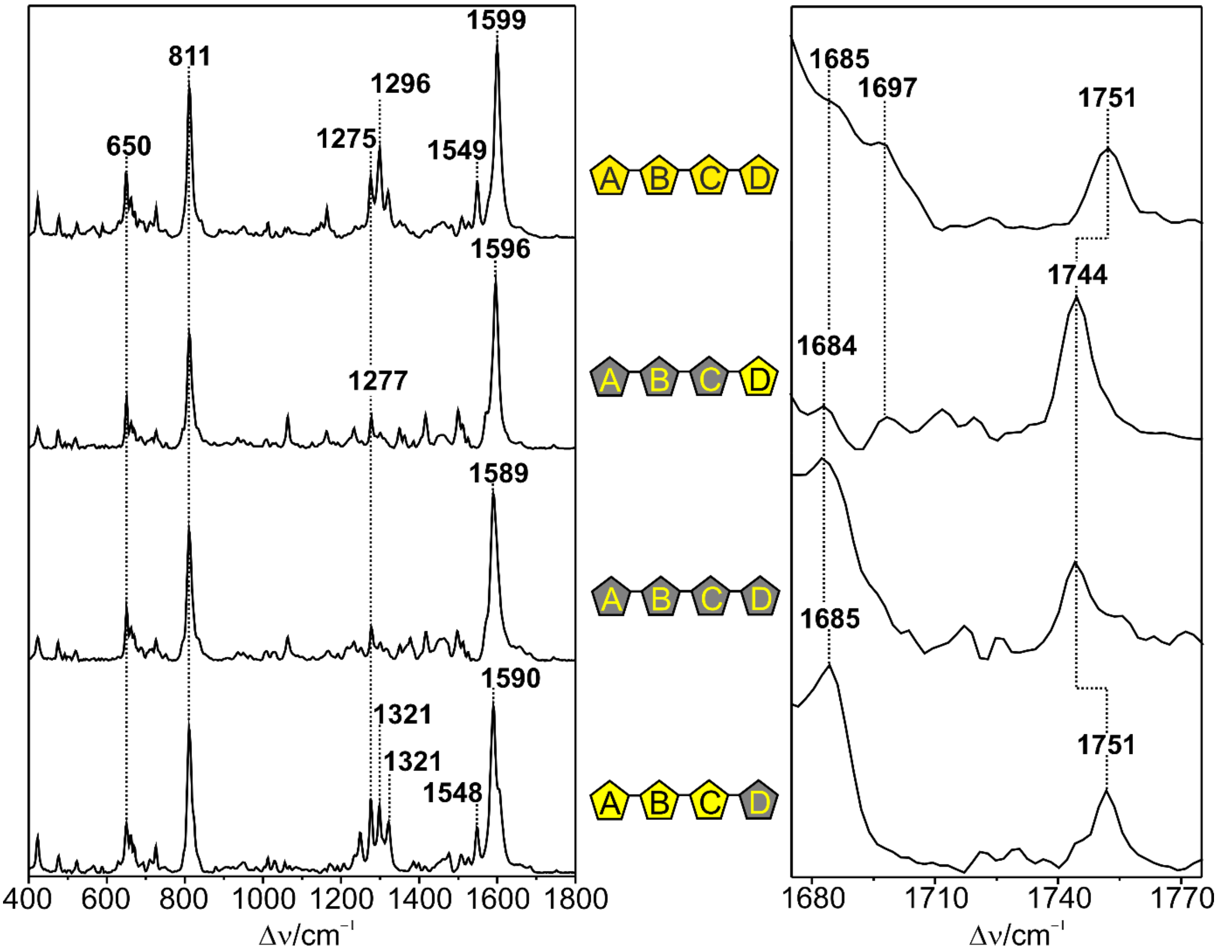

Figure S2. RR of Pfr with different H/D patterns at the pyrrole rings A, B, C vs. D, the ring C protonated propionic side chain. The frequencies in the C=O stretching region (right panel) agree very well with the IR data and thus confirm the assignments given in Table 1 of the manuscript.

2. RR spectra of Lumi-F

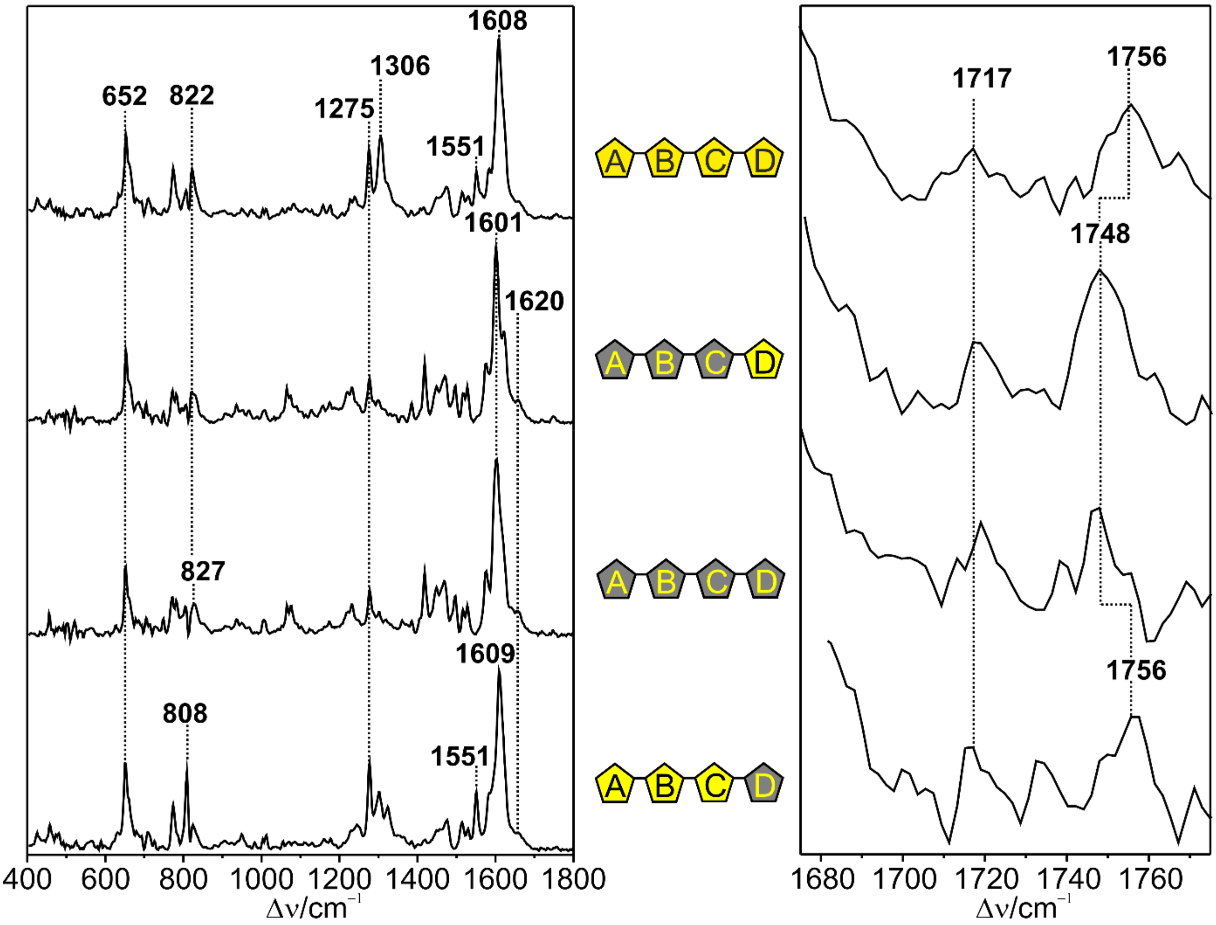

Figure S3. RR of Lumi-F with different H/D patterns at the pyrrole rings A, B, C vs. D, the ring C protonated propionic side chain. The frequencies in the C=O stretching region (right panel) agree very well with the IR data and thus confirm the assignments given in Table 1 of the main paper.

3. RR spectra of Pfr´

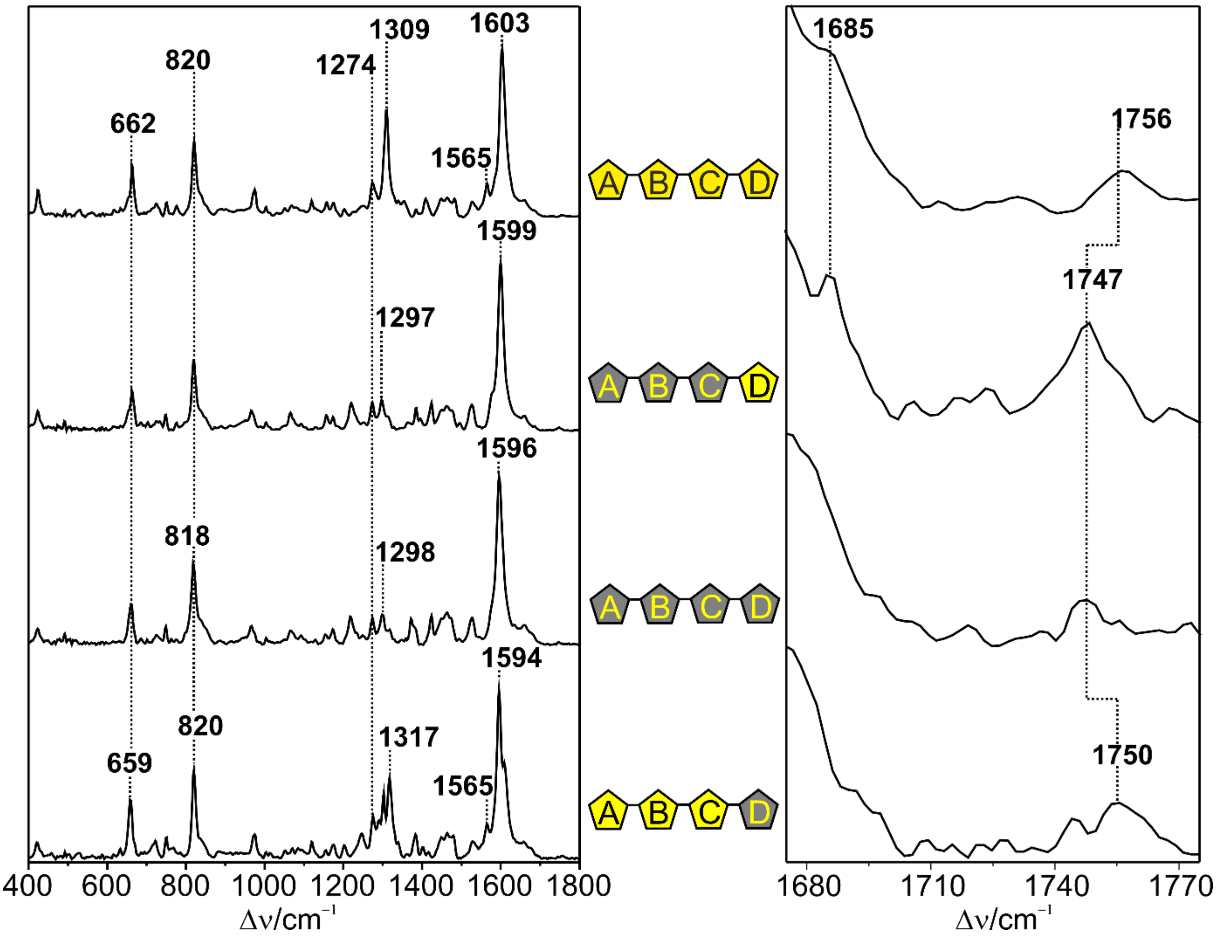

Figure S4. RR of Pfr´ (see Figure S1) with different H/D patterns at the pyrrole rings A, B, C vs. D, the ring C protonated propionic side chain.

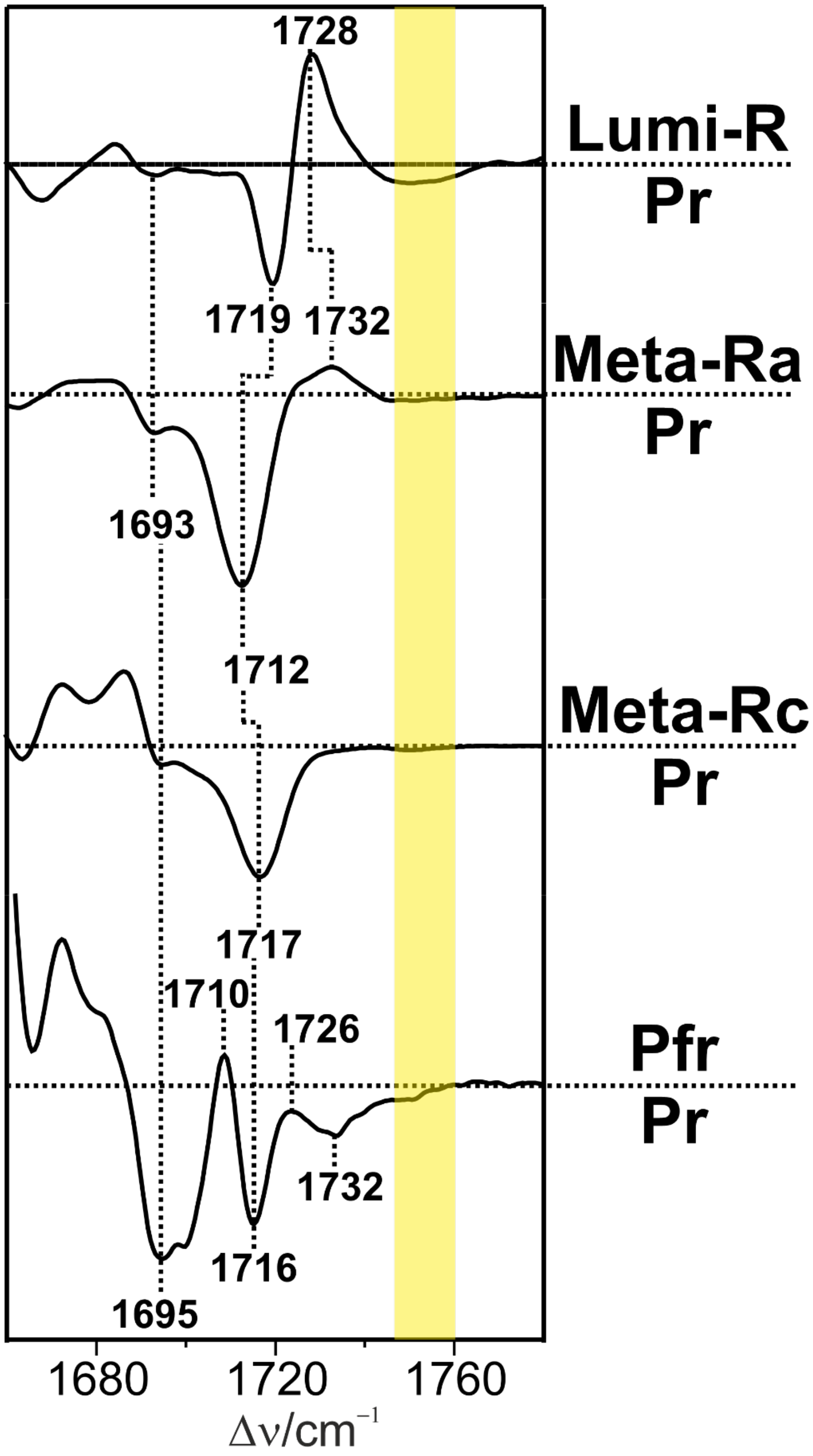

Figure S5. IR difference spectra of the Pr → Pfr reaction pathway of Agp1 in H_2O (see Figure S1) in the C=O stretching region. The yellow rectangle marks the region expected for a protonated propionic side chain, show no indication for a negative or positive signal. The horizontal dotted lines in the IR difference spectra mark the intensity difference of zero.

References

1 F. Velázquez Escobar, D. Buhrke, N. Michael, L. Sauthof, S. Wilkening, N. N. Tavraz, J. Salewski, N. Frankenberg-Dinkel, M. A. Mroginski, P. Scheerer, T. Friedrich, F. Siebert and P. Hildebrandt, *Photochem. Photobiol.*, 2017, **93**, 724–732.

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