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Supplemental Information

Retinal Configuration of *pp*R Intermediates Revealed by Photoirradiation Solid-State NMR and DFT

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Table S1. ^{13}C NMR chemical shift values of [14, 20-^{13}C] Ret in retinal binding microbial proteins [ppm]

		20-^{13}C	14-^{13}C	Configuration	Ref.
*pp*R (0°C)	G-state	13.3		13-*trans*, 15-*anti*	(1)
	M-intermediate	22.3		13-*cis*, 15-*anti*	(1)
*pp*R (-20°C)	G-state	13.5		13-*trans*, 15-*anti*	(1)
	M-intermediate	24.1, 22.5, 21.7		13-*cis*, 15-*anti*	(1)
*pp*R (-40°C)	G-state	13.5	121.7	13-*trans*, 15-*anti*	
	M-intermediate	22.3	126.8	13-*cis*, 15-*anti*	
*pp*R (-60°C)	G-state	13.6	121.6	13-*trans*, 15-*anti*	
	O-intermediate	16.4	115.4	13-*trans*, 15-*syn*	
	M-intermediate	22.6	127.1	13-*cis*, 15-*anti*	
	N'-intermediate	23.9	115.4	13-*cis*	
*pp*R/pHtrII (0°C)	G-state	13.6		13-*trans*, 15-*anti*	(1)
	M-intermediate	22.7		13-*cis*, 15-*anti*	(1)
*pp*R/pHtrII (-20°C)	G-state	13.5		13-*cis*, 15-*anti*	(1)
	M-intermediate	23.5, 22.3, 21.3		13-*cis*, 15-*anti*	(1)
*pp*R/pHtrII (-40°C)	G-state	13.5		13-*trans*, 15-*anti*	
	O-intermediate	16.1		13-*trans*	
	M-intermediate	22.1, 22.9		13-*cis*, 15-*anti*	
	N'-intermediate	23.9		13-*cis*	
SrSRI (-40°C)	G-state	13.8		13-*trans*, 15-*anti*	(2)
	M-intermediate	19.8		13-*cis*	(2)
	P-intermediate	24.8		13-*cis*, 15-*anti*	(2)
bR	bR(568)(AT)	13.3	122.0	13-*trans*, 15-*anti*	(3)
	bR(568)(CS)	22.0	110.5	13-*cis*, 15-*syn*	(3)
	M_0	21.5	124.5	13-*cis*, 15-*anti*	(4)
		19.5		13-*cis*, 15-*anti*	(5)
	M_n	17.8[a]	124.6[b]	13-*cis*, 15-*anti*	(5)
					(6)
	N		115.2	13-*cis*, 15-*anti*	(7)
bR (Y185F)	AT	13.2	123.1	13-*trans*, 15-*anti*	(8)
	CS	21.7	110.0	13-*cis*, 15-*syn*	(8)
	CS*	18.0	115.3	13-*cis*, 15-*syn*	(8)
	N	19.2	125.4	13-*cis*, 15-*anti*	(8)
	O	13.2	123.1	13-*trans*, 15-*anti*	(8)

[a]Ref. (5).
[b]Ref. (6).

Table S2. The basis set dependence of the calculation of chemical shift examined for G-state of retinal using several basis sets.

	^{13}C NMR chemical shift values [ppm]	
Base set	14-^{13}C retinal	20-^{13}C retinal
6-311G	129.4	18.9
6-311G*	126.8	17.6
6-311G**	128.0	18.2
6-311+G**	127.9	17.4

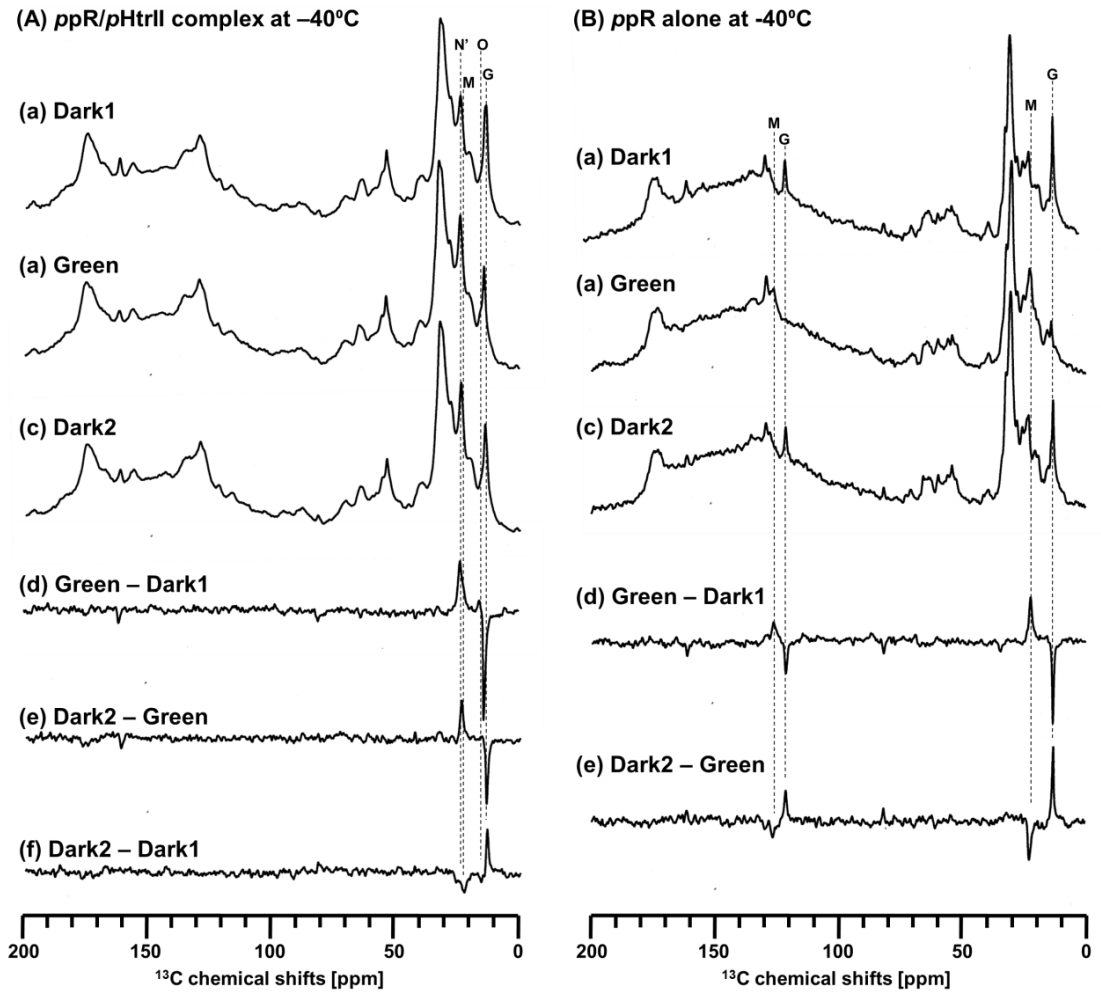

Figure S1. A. ^{13}C CP-MAS NMR spectra and these difference spectra of the [20-^{13}C] retinal labeled *p*pR/*p*HtrII complex at -40 °C using 4 kHz MAS. The range of these spectra was from 0 ppm to 200 ppm. 1D ^{13}C CP MAS NMR spectra (a) acquired under initial dark conditions (Dark1), (b) acquired under irradiation with green light state (520 nm) (Green) and (c) obtained one day after turning off irradiation (dark2). And these difference spectra (d) obtained by subtracting Dark1 from Green (Green – Dark1), (e) obtained by subtracting Green from Dark2 (Dark2 – Green), and (f) obtained by subtracting Dark1 from Dark2 (Dark2 – Dark1). B. ^{13}C CP-MAS NMR spectra and these difference spectra of the [14,20-^{13}C] retinal labeled *p*pR alone without *p*HtrII at -40 °C using 4 kHz MAS. The range of these spectra was from 0 ppm to 200 ppm. 1D ^{13}C CP MAS NMR spectra (a) acquired under initial dark conditions (Dark1), (b) acquired under irradiation with green light state (Green) and (c) obtained one day after turning off irradiation (Dark2). And these difference spectra (d) obtained by subtracting Dark1 from Green (Green – Dark1), (e) obtained by subtracting Green from Dark2 (Dark2 – Green).

Supporting References

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