

1 **SUPPORTING MATERIAL**

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3 **Retinal configuration of *ppR* intermediates revealed by photo-irradiation**

4 **solid-state NMR and DFT**

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

21 **microbial proteins [ppm]**

		20- ^{13}C	14- ^{13}C	Configuration	Ref.
<i>ppR</i> (0°C)	G-state	13.3		13- <i>trans</i> , 15- <i>anti</i>	(1)
	M-intermediate	22.3		13- <i>cis</i> , 15- <i>anti</i>	(1)
<i>ppR</i> (-20°C)	G-state	13.5		13- <i>trans</i> , 15- <i>anti</i>	(1)
	M-intermediate	24.1, 21.7	22.5,	13- <i>cis</i> , 15- <i>anti</i>	(1)
<i>ppR</i> (-40°C)	G-state	13.5	121.7	13- <i>trans</i> , 15- <i>anti</i>	
	M-intermediate	22.3	126.8	13- <i>cis</i> , 15- <i>anti</i>	
<i>ppR</i> (-60°C)	G-state	13.6	121.6	13- <i>trans</i> , 15- <i>anti</i>	
	O-intermediate	16.4	115.4	13- <i>trans</i> , 15- <i>syn</i>	
	M-intermediate	22.6	127.1	13- <i>cis</i> , 15- <i>anti</i>	
	N'-intermediate	23.9	115.4	13- <i>cis</i>	
<i>ppR/pHtrII</i> (0°C)	G-state	13.6		13- <i>trans</i> , 15- <i>anti</i>	(1)
	M-intermediate	22.7		13- <i>cis</i> , 15- <i>anti</i>	(1)
<i>ppR/pHtrII</i> (-20°C)	G-state	13.5		13- <i>cis</i> , 15- <i>anti</i>	(1)
	M-intermediate	23.5, 21.3	22.3,	13- <i>cis</i> , 15- <i>anti</i>	(1)
<i>ppR/pHtrII</i> (-40°C)	G-state	13.5		13- <i>trans</i> , 15- <i>anti</i>	
	O-intermediate	16.1		13- <i>trans</i>	
	M-intermediate	22.1, 22.9		13- <i>cis</i> , 15- <i>anti</i>	
	N'-intermediate	23.9		13- <i>cis</i>	
SrSRI	G-state	13.8		13- <i>trans</i> , 15- <i>anti</i>	(2)

(-40°C)					
	M-intermediate	19.8		13- <i>cis</i>	(3)
	P-intermediate	24.8		13- <i>cis</i> , 15- <i>anti</i>	(3)
bR	bR(568)(AT)	13.3	122.0	13- <i>trans</i> , 15- <i>anti</i>	(4)
	bR(568)(CS)	22.0	110.5	13- <i>cis</i> , 15- <i>syn</i>	(4)
	M ₀	21.5	124.5	13- <i>cis</i> , 15- <i>anti</i>	(5)
		19.5		13- <i>cis</i> , 15- <i>anti</i>	(6)
	M _n	17.8 ^{a)}	124.6 ^{b)}	13- <i>cis</i> , 15- <i>anti</i>	^{a)} (6)
					^{b)} (5)
	N		115.2	13- <i>cis</i> , 15- <i>anti</i>	(7)
bR (Y185F)	AT	13.2	123.1	13- <i>trans</i> , 15- <i>anti</i>	(8)
	CS	21.7	110.0	13- <i>cis</i> , 15- <i>syn</i>	(8)
	CS*	18.0	115.3	13- <i>cis</i> , 15- <i>syn</i>	(8)
	N	19.2	125.4	13- <i>cis</i> , 15- <i>anti</i>	(8)
	O	13.2	123.1	13- <i>trans</i> , 15- <i>anti</i>	(8)

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