ELECTRONIC SUPPLEMENTARY INFORMATION

The UV-Visible Action-Absorption Spectrum of All-*trans* and 11-*cis* Protonated Schiff Base Retinal in the Gas Phase

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TABLE S1. Relative energies ΔE and twist angles β of the 6s-*trans* and 6s-*cis* rotomers at the equilibrium geometries of the all-*trans* protonated Schiff base retinal (PSBR) chromophore calculated at different levels of theory. We note that the relative energies of the rotomers are very sensitive to the computational method. The values of the twist angles vary in a smaller range, with the largest deviation being $\sim 10°$. In the present work, the PBE0/cc-pVDZ equilibrium geometries of the 6s-*trans* and 6s-*cis*$(-)$ rotomers are used for calculating vertical excitation energies of all-trans as well as 11-cis PSBR.

all-*trans*	6s-*trans*		6s-*cis*$(-)$		6s-*cis*$(+)$	
	ΔE (meV)	β	ΔE (meV)	β	ΔE (meV)	β
PBE0/cc-pVDZ	0	172°	+39	−38°	+22	+32°
MP2/cc-pVTZ	0	171°	+19	−42°	+0.5	+38°
MRMP2/cc-pVTZ//MP2/cc-pVTZ	0	171°	−24	−51°	−49	+48°

TABLE S2. Leading electronic configurations of the first five XMCQDPT2[15]/SA(5)-CASSCF(12,12)/cc-pVDZ electronic wavefunctions and their weights for the 6s-*trans* and 6s-*cis* rotomers of the 11-*trans* (all-*trans*) and 11-*cis* PSBR chromophores. We note that leading electronic configurations are similar for the two isomers; however, the contributions from other configurations with smaller weights may vary significantly. In particular, there is a pronounced admixture of about 1% of the 2nd electronic configuration, which correlates with the HOMO→LUMO transition, to the S_3 excited state in the case of the 11-*cis* PSBR isomer, which explains a higher oscillator strength for the S_0→S_3 excitation compared to that of the 11-*trans* isomer. This gives rise to the increased absorption for 11-*cis* PSBR in the 380–320 nm region.

			11-*trans*		11-*cis*	
			6s-*cis*	6s-*trans*	6s-*cis*	6s-*trans*
S_0	1	222222000000	0.73	0.71	0.73	0.72
S_1	2	222221100000	0.61	0.59	0.60	0.60
S_2	29	222212100000	0.35	0.21	0.35	0.27
	8	222220200000	0.24	0.29	0.23	0.27
	3	222221010000	0.07	0.12	0.08	0.12
S_3	29	222212100000	0.28	0.34	0.29	0.34
	8	222220200000	0.09	0.03	0.09	0.04
	3	222221010000	0.16	0.15	0.18	0.17
	35	222211200000	0.08	0.08	0.07	0.07
S_4	337	222122100000	0.33	0.25	0.33	0.30
	3	222221010000	0.09	0.06	0.09	0.06
	9	222220110000	0.05	0.10	0.06	0.09
	35	222211200000	0.07	0.08	0.08	0.10

TABLE S3. Calculated vertical excitation energies, transition wavelength, and oscillator strengths for all-*trans* retinal, done at the XMCQDPT2[15]/SA(5)-CASSCF(12,12)/cc-pVDZ level of theory at the PBE0/cc-pVDZ equilibrium geometry. Considered are here transitions from the first singlet excited state S_1. For computational details see Table 1 in the main text.

11-*trans*	6s-*trans*			6s-*cis*		
	E (eV)	λ (nm)	$f_{\text{osc.}}$	E (eV)	λ (nm)	$f_{\text{osc.}}$
$S_1 \rightarrow S_2$	0.83	1489.6	7.22e-3	0.94	1318.5	1.86e-2
$S_1 \rightarrow S_3$	1.65	751.0	3.94e-1	1.44	860.5	4.15e-1
$S_1 \rightarrow S_4$	1.98	627.8	9.61e-2	2.01	615.6	7.71e-2
$S_1 \rightarrow S_5$	2.37	522.2	9.41e-1	2.33	531.1	5.38e-1
$S_1 \rightarrow S_6$	2.63	472.3	1.62	2.59	479.4	1.03e-1
$S_1 \rightarrow S_7$	2.80	442.2	3.07e-2	2.71	458.2	1.55
$S_1 \rightarrow S_8$	3.06	405.1	1.65e-3	2.98	416.0	3.33e-2
$S_1 \rightarrow S_9$	3.17	391.6	1.25e-3	3.24	382.6	1.28e-3
$S_1 \rightarrow S_{10}$	3.63	368.6	2.72e-3	3.30	376.0	8.70e-4
$S_1 \rightarrow S_{11}$	3.56	348.4	3.04e-5	3.46	358.0	1.52e-2
$S_1 \rightarrow S_{12}$	3.94	314.4	2.45e-3	3.99	310.6	3.14e-3
$S_1 \rightarrow S_{13}$	4.11	301.5	4.70e-3	4.10	302.6	1.99e-3
$S_1 \rightarrow S_{14}$	4.39	282.3	5.78e-4	4.34	285.7	2.51e-3

TABLE S4. Calculated vertical excitation energies, transition wavelength, and oscillator strengths for 11-*cis* retinal, done at the XMCQDPT2[15]/SA(5)-CASSCF(12,12)/cc-pVDZ level of theory at the PBE0/cc-pVDZ equilibrium geometry. Considered are here transitions from the first singlet excited state S_1. For computational details see Table 1 in the main text.

11-*cis*	6s-*trans*			6s-*cis*		
	E (eV)	λ (nm)	$f_{osc.}$	E (eV)	λ (nm)	$f_{osc.}$
$S_1 \rightarrow S_2$	0.90	1371.8	2.82e-3	0.94	1318.0	1.96e-2
$S_1 \rightarrow S_3$	1.61	768.6	4.50e-1	1.44	856.2	3.92e-1
$S_1 \rightarrow S_4$	1.99	621.7	4.67e-2	2.01	614.9	5.11e-2
$S_1 \rightarrow S_5$	2.37	523.2	4.63e-1	2.33	532.0	3.87e-1
$S_1 \rightarrow S_6$	2.62	472.9	1.88	2.59	483.1	4.11e-2
$S_1 \rightarrow S_7$	2.78	446.0	2.69e-2	2.71	469.0	1.44
$S_1 \rightarrow S_8$	2.96	418.6	9.91e-3	2.98	419.1	8.48e-2
$S_1 \rightarrow S_9$	3.17	391.7	7.59e-3	3.24	383.2	4.62e-3
$S_1 \rightarrow S_{10}$	3.40	363.8	7.43e-3	3.30	376.4	1.01e-2
$S_1 \rightarrow S_{11}$	3.54	350.7	1.23e-3	3.46	359.7	8.62e-3
$S_1 \rightarrow S_{12}$	4.01	309.1	7.57e-4	3.99	311.2	2.70e-3
$S_1 \rightarrow S_{13}$	4.12	301.0	3.57e-3	4.10	305.0	1.60e-3
$S_1 \rightarrow S_{14}$	4.49	275.9	3.20e-5	4.34	283.6	7.77e-4