Supporting Information

Electronic Excited States of Carotenoid Dyes Adsorbed on TiO_2

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The following procedure was performed in order to partially account for the presence of low energy spectral form which contributes weakly to the absorption, but significantly stronger to the electroabsorption, and and to assess quantitatively the value of Δμ for this form. Let us call the absorption and electroabsorption spectra with no acid added as A_0% and D_0%, and the spectra of free ATRA as A_ATRA, D_ATRA.

1. The absorption spectrum at a given acid content (X%) was fitted with a linear combination of the redshifted absorption spectrum of ATRA@TiO2 at 0% acid and the absorption spectrum of free ATRA:

$$A\_X\% = c_1 \cdot A\_0\%(-\text{shift}) + c_2 \cdot A\_ATRA \quad (S1)$$

2. Analogously, the corresponding electroabsorption spectrum was fitted with a linear combination of the redshifted electroabsorption of ATRA@TiO2 at 0% acid and the electroabsorption of free ATRA:

$$D\_X\% = d_1 \cdot D\_0\%(-\text{shift}) + d_2 \cdot D\_ATRA \quad (S2)$$

If the ratio c_1/c_2 were the same a d_1/d_2 then it could be said that the long wavelength forms are represented in the electroabsorption spectrum strictly proportional to their contribution to the absorption. In the following it should be kept in mind that the electrochromism of adsorbed pigments consist merely of the second derivative of absorption. Thus if the ratio of fit coefficients is not the same in absorption and electroabsorption spectra, then the ratio:

$$\frac{d_1/d_2}{c_1/c_2} \quad (S3)$$

represents the difference between the coefficient a_2 (and thus Δμ) for the low energy form relative to the a_2 and Δμ obtained from the mean fit at 0% acid. More specifically, the ratio of Δμ's is the square root of the above expression.

The fits of absorption and electroabsorption spectra were performed for both ATRA and bixin at different acid contents and the results are shown in Figs. S1 and S2. Electroabsorption spectra are normalized to the same electric field intensity 1E5 V/cm. The thin lines are the experimental spectra and the thick dashed lines are the fits optimized with respect to the red shift of one of the fit components.

The results of the fitting procedure are collected in Table S1. The mean values in the last column indicate the always higher contribution of the low energy form if we adjust its red shift in the electroabsorption spectra. The mean ratio in the last column translates into ≈1.16 times larger values of Δμ for ATRA and bixin. A separate assessment of the electrochromism of the low energy form would give larger increases in Δμ.

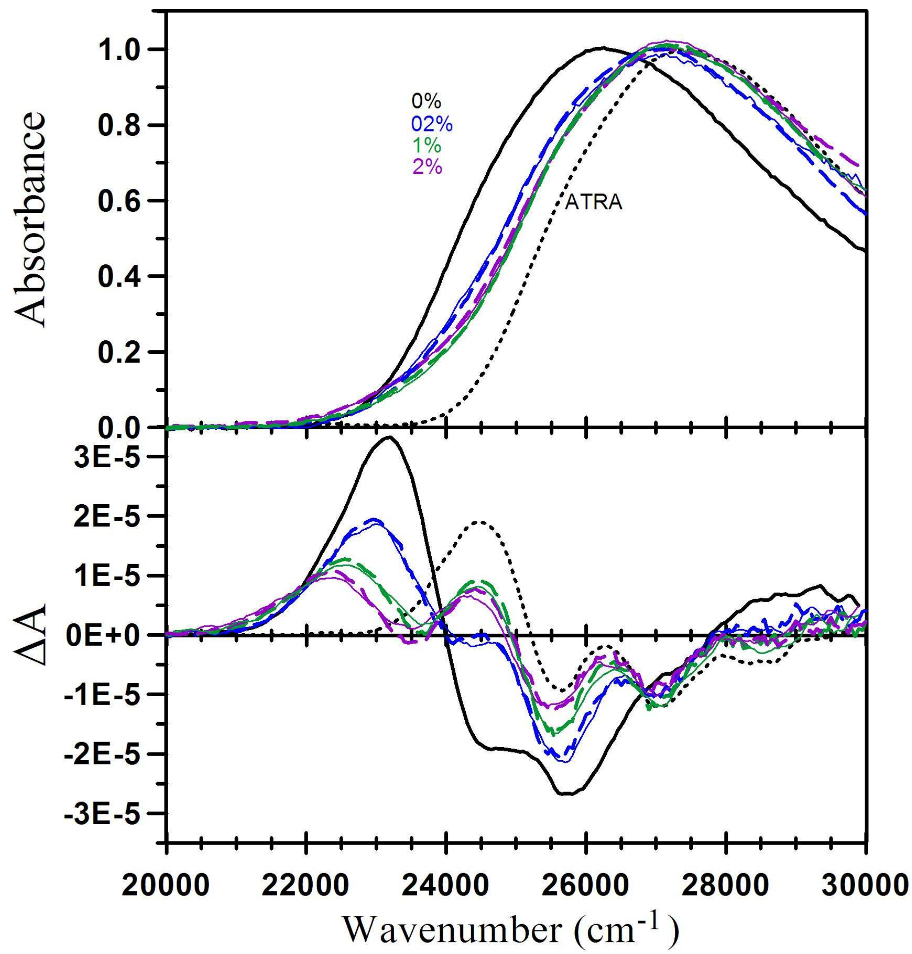

Fig. S1. Fit results for all-trans retinoic acid (ATRA) at TiO_2 in the presence of acetic acid (concentrations indicated in the figure).

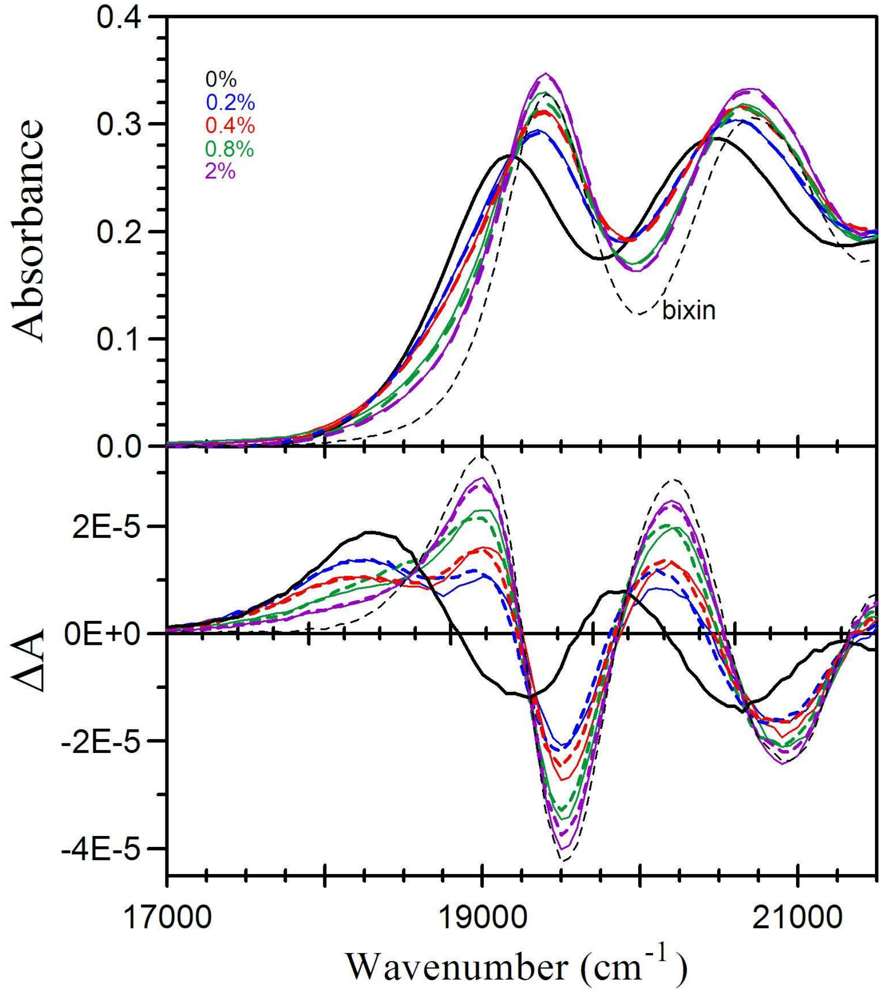

Fig. S2. Fit results for bixin@TiO_2 in the presence of acetic acid (concentrations indicated in the figure).

Table S1

ATRA @ TiO_2	(c_1/c_2) (d_1/d_2)	$(d_1/d_2)/(c_1/c_2)$
A_0.2% = 0.447*A_0%(-250) + 0.605*A_ATRA D_0.2% = 0.566*D_0%(-250) + 0.564*D_ATRA	0.739 1.003	1.357
A_1% = 0.260*A_0%(-600) + 0.805*A_ATRA D_1% = 0.375*D_0%(-600) + 0.864*D_ATRA	0.323 0.434	1.343
A_2%B = 0.261*A_0%(-800) + 0.820*A_ATRA D_2%B = 0.310*D_0%(-800) + 0.731*D_ATRA	0.317 0.436	1.375
		mean: 1.358
BIXIN @ TiO_2		
A_0.2% = 0.532*A_0%(-150) + 0.564*A_BIXIN D_0.2% = 0.650*D_0%(-150) + 0.550*D_BIXIN	0.943 1.182	1.253
A_0.4% = 0.427*A_0%(-200) + 0.704*A_BIXIN D_0.4% = 0.48*D_0%(-200) + 0.630*D_BIXIN	0.606 0.762	1.257
A_0.8% = 0.277*A_0%(-200) + 0.816*A_BIXIN D_0.8% = 0.400*D_0%(-200) + 0.750*D_BIXIN	0.339 0.533	1.572
A_2% = 0.177*A_0%(-250) + 0.953*A_BIXIN D_2% = 0.211*D_0%(-200) + 0.902*D_BIXIN	0.186 0.234	1.258
		mean: 1.335