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Picosecond Laser Induced Electric Field Modulation of Carotenoid Absorption Bands

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The formation of an intense electric field created by light induced charge separation is shown to induce an electrochromic band shift in an electronically isolated carotene molecule.

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Observation of band shifts in the absorption spectra of *in vivo* carotenoids has been attributed to electric field effects generated by membrane potentials. This electrochromism is related to what is known as the Stark effect, a term which is used to describe the effect of an applied electric field on many physical processes. Previous *in vitro* studies of how electric fields effect the absorption spectra of molecules all have relied on applying the perturbing electric field by using external electrodes around a dielectric spacer containing the molecule to be studied. The maximum applied field in these examples has been between 0.5 MV/cm and 3 MV/cm. These electric field intensities are of the same magnitude as those thought to be present across the membranes studied in the *in vivo* experiments.

Here we present a new and unique way of forming an intense electric field near a molecule in order to induce electrochromism. We have done this by creating an electron-hole pair within close proximity to, but electronically isolated from, a polarizable molecule. The molecular system that we have utilized is shown in Figure 1. It consists of a zinc porphyrin - pyromellitic diimide light induced charge transfer complex held rigidly proximate to a β -carotene using a calix[4]arene linkage. The formation of the charge separated state of the porphyrin-diimide results in a dipole formed by the 8.4 Å separation of the electron-hole pair. The electric field from this dipole was found to induce electrochromism in the carotene.

In order to detect the electrochromism we have synthesized three calix[4]arene based molecules. The complete molecule as shown in figure 1 as well as control molecules, one containing just the calix[4]arene and porphyrin-diimide and one containing just the calix[4]arene and carotene.

The lifetime of the charge separated state was found to be 3.7 ns in toluene. Transient absorption spectra of all of the molecules were recorded 150 ps after the formation of the charge separated state by a 200 fs pump pulse at 420 nm. To detect any change in the ground state absorption

Figure 1. Molecule used to study electrochromism.

spectrum of the carotene due to the presence of the electric field, a difference spectrum was calculated using transient spectra of the full molecule and the molecule containing only the porphyrin-diimide side chain. Absorption bands that were found to occur only in the charge transfer state of the porphyrin-diimide and which were well removed from the ground state absorption bands of the carotenoid were used to insure that the difference spectra did not contain artifacts due to differences in pump absorption between samples.

In order to change the electric field strength at the carotene, the dielectric constant of the solvent was changed over an order of magnitude by using mixtures of toluene and benzonitrile. Figure 2 shows the difference spectra between the full molecule and the porphyrin-diimide only molecule in toluene, 5% benzonitrile, 10% benzonitrile, and in neat benzonitrile. The Stark shift of the carotenoid absorption band resulted in a derivative shaped difference spectrum. Only part of the negative going ΔA band (below 450 nm) can be seen in figure 2 whereas the positive going lobe is clearly seen in the neat toluene through 20% benzonitrile spectra. As the dielectric constant of the solvent mixture increased the electrochromic shift decreased until it was virtually nonexistent in neat benzonitrile.

Figure 2: Absorption changes due to laser induced electric field.

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