

Ultrafast E to Z Photoisomerization of Chiral Biomimetic Molecular Switches

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Abstract: Transient absorption spectroscopy on chiral biomimetic molecular switches reveals a critical and novel influence of methyl substitutions on the photoreaction speed and on the observation of vibrational coherence in both isomerization directions.

Introduction. Biomimetic molecular switches based on the N-alkylated indanylidene-pyrroline (NAIP) structure have been designed to mimic the ultrafast, vibrationally coherent cis-trans photoisomerization observed in rhodopsin [1]. Using ultrafast transient absorption spectroscopy and state-of-the-art modeling, it was demonstrated that in solution these molecules undergo an ultrafast photoisomerization in which a significant amount of mechanical energy is delivered into a few specific vibrational modes such that vibrational wavepackets are observed during the photoreaction [2-4].

Newly-synthesized chiral (Ch) NAIP compounds (see Fig. 1A and 1B) are available in which a H atom replaces one of the two methyl groups carried by the C₂ atom in the previous, non-chiral NAIP's. Here, we apply transient absorption spectroscopy with a 400-nm, 60-fs pump and a UV-VIS supercontinuum probe to study the E to Z photoisomerization dynamics in methanol of a racemic mixture of the chiral Ch-MeO-NAIP and Ch-dMe-MEO-NAIP. In the latter, the methyl group on C₅ in the pyrrolinium moiety is also replaced by a H atom. We observe that the number of methyl groups either on C₂ or on C₅ seems to control the speed of the E to Z photoisomerization around the C₁=C₄ double bond as well as the occurrence of vibrational coherence along the photoreaction. However preliminary results on the reverse Z to E photoreaction indicate a very fast photoreaction for the Ch-MeO-NAIP (Z), somewhat weakening the generality of this conclusion also made in a recent investigation of methyl substitutions of the protonated Schiff base retinal in solution [5].

Results. In the chiral Ch-dMe-MeO-NAIP (Fig. 1D) the Excited State Absorption (ESA) spectrum almost perfectly overlaps the Ground State Bleach (GSB) which is thus non apparent at short time delays, but is detected as a weak negative signal between 350 and 400 nm at later delays (> ~1 ps). Instead, for the chiral Ch-MeO-NAIP (Fig. 1C), the overlap between ESA and GSB is partial. The spectroscopic signature of the Photoproduct Absorption (PA) emerges after ~ 0.5 ps in the range 400 to 450 nm. For Ch-dMe-MeO-NAIP the ESA and PA are spectrally separated, while in the case of the chiral MeO-NAIP the PA appears in the continuity of the ESA, as a unique band which would red-shift after ~0.5 ps. After ~30 ps, a quasi-static, vibrationally-relaxed spectrum is observed for both molecules which overlaps with the difference between the pure Z and pure E static spectra (not shown). Quantitative analysis reveals bi-exponential decay of the SE signal in both cases, with time constants of ~ 0.6 ps and ~ 1.6 ps and relative amplitudes 60% and 40% respectively for the Ch-dMe-MeO-NAIP and of ~ 0.4 ps (50%) and 1.3 ps (50%) for the Ch-MeO-NAIP.

Discussion. The above results show that both chiral photoswitches display a photoreaction kinetics qualitatively different from that of the parent (non-chiral) MeO-NAIP, but very similar to that of the non-chiral dMe-MeO-NAIP. The parent MeO-NAIP displays several signatures of a vibrationally coherent photoreaction (see e.g. [3]), including a far red-shifting SE impulsively followed by the far-red-detuned early PA signature (see Fig1. D). The rapid cross over from SE to PA after ~220 fs (See Fig. 1.F) in the red part of the spectrum is attributed to the signature of a vibrational wavepacket travelling through the conical intersection and is thus considered as a measurement of the Excited State Lifetime (ESL) whenever vibrational coherence signature is observed [2-4]. Here instead, no signature of vibrational coherence is observed for the chiral molecules excited in the same conditions, and neither for the non chiral dMe-MeO-NAIP [6, 7]. All kinetic traces may be adjusted by exponential decay curves as would be expected for an incoherent photoreaction modeled by rate equations. In particular, the SE decay is significantly slower and bi-exponential, and no short-lived broad PA signature above 500 nm is observed in contrast to the parent MeO-NAIP. Thus the estimate of ESL arises from a different kinetic picture and the few hundred femtoseconds exponential-decaying time constants reveal a significantly longer ESL for the C₂-chiral molecules as well as for the non-chiral but C₅-demethylated dMe-MeO-NAIP.

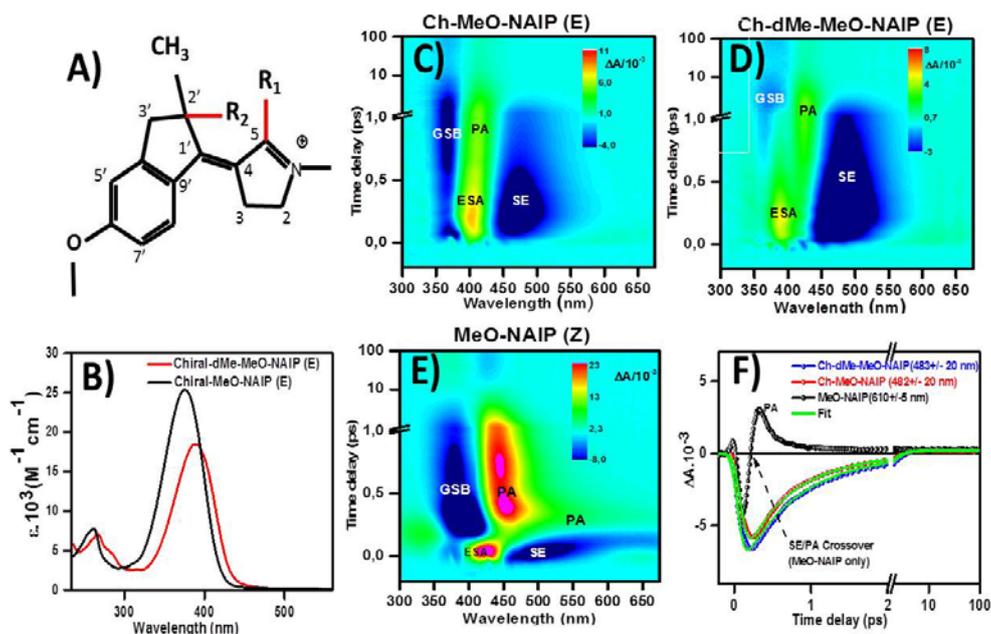


Fig. 1 (A) Chemical structure of the NAIP molecular switches: R2=H = chiral; R2= Me = non chiral; R1 = H = “demethylated”; R1=CH3 otherwise. (B) Steady-state absorption spectra of the *E* Ch-dMe-MeO-NAIP (red), and *E* Ch-MeO-NAIP (black) in MeOH. (C), (D) and (E) UV-VIS transient absorption data for Ch-dMe-MeO-NAIP, Ch-MeO-NAIP and MeO-NAIP in methanol. (F) Transient absorption kinetics at selected wavelengths showing the SE decay in the red part of the observation window, followed (MeO-NAIP) or not (the other two) by the impulsive PA signature.

Conclusion. The results above indicate that removing one methyl substituent in C₂ (chiral molecules) or in C₅ (so-called “demethylated”) significantly reduces the *E* to *Z* photoreaction speed, and washes out all signatures of vibrationally coherent reactive motion as observed in both isomerization directions (*Z* to *E* and *E* to *Z*) in the parent MeO-NAIP carrying two methyl groups on C₂ and one on C₅. This is tentatively interpreted as a modification of the height of a putative potential energy barrier on the S1 potential energy surface (PES), controlled by methyl substitutions on C₂ and C₅. Preliminary results on the reverse (*Z* to *E*) isomerization reaction in the chiral molecules (not shown) indicate a much faster photoreaction speed and the recovery of wavepacket signatures for the *Z*-Ch-MeO-NAIP, showing an isomer-dependent influence of the methyl substitutions. A quantitative understanding based on computed excited state trajectories is in progress.

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