Supplemental Information

Dependence of the solid-state photomechanical response of 4-chlorocinnamic acid on crystal shape and size

Taehyung Kim, Lingchao Zhu, Leonard J. Mueller and Christopher J. Bardeen*

Department of Chemistry, University of California, Riverside, CA 92521, U.S.A. Email: christopher.bardeen@ucr.edu; Fax: +1-951-827-4713; Phone: +1-951-827-2723.

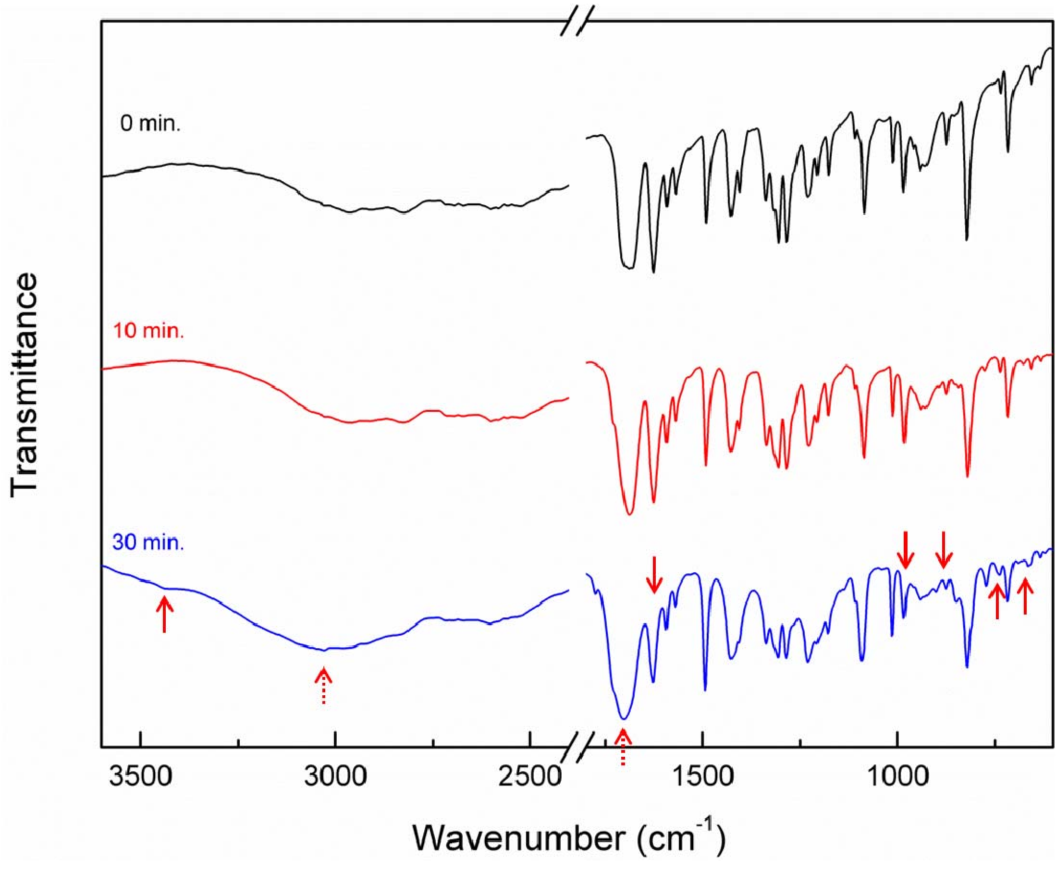

Figure S1. Infrared spectra of 4Cl-CA microcrystals under UV exposure for 0 minutes (top, black), 10 minutes (middle, red), and 30 minutes (bottom, blue) (KBr pallet, room temperature). As the photoreaction progresses, the aliphatic C=C stretching mode (1620 cm^{-1}) decreases and the cyclobutane ring deformation vibrations (672 and 745 cm^{-1}) increase, indicating [2+2] photodimerization. Disruption of the hydrogen-bonding network in the **4Cl-CA** crystal by photoreaction is inferred from the decrease in the peak at 942 cm^{-1} (O-H deformation out of plane), the shift and broadening of the peak at 1700 cm^{-1}

(C=O stretching), the shift of the broad peak around 2970 cm^{-1} (O-H stretching) to higher frequency, and the appearance of a new peak at 3440 cm^{-1} suggestive of free OH groups. All these changes are marked by arrows (solid arrows for appearing or diminishing peaks and dotted arrows for shifting peaks) in the 30 minute spectrum.

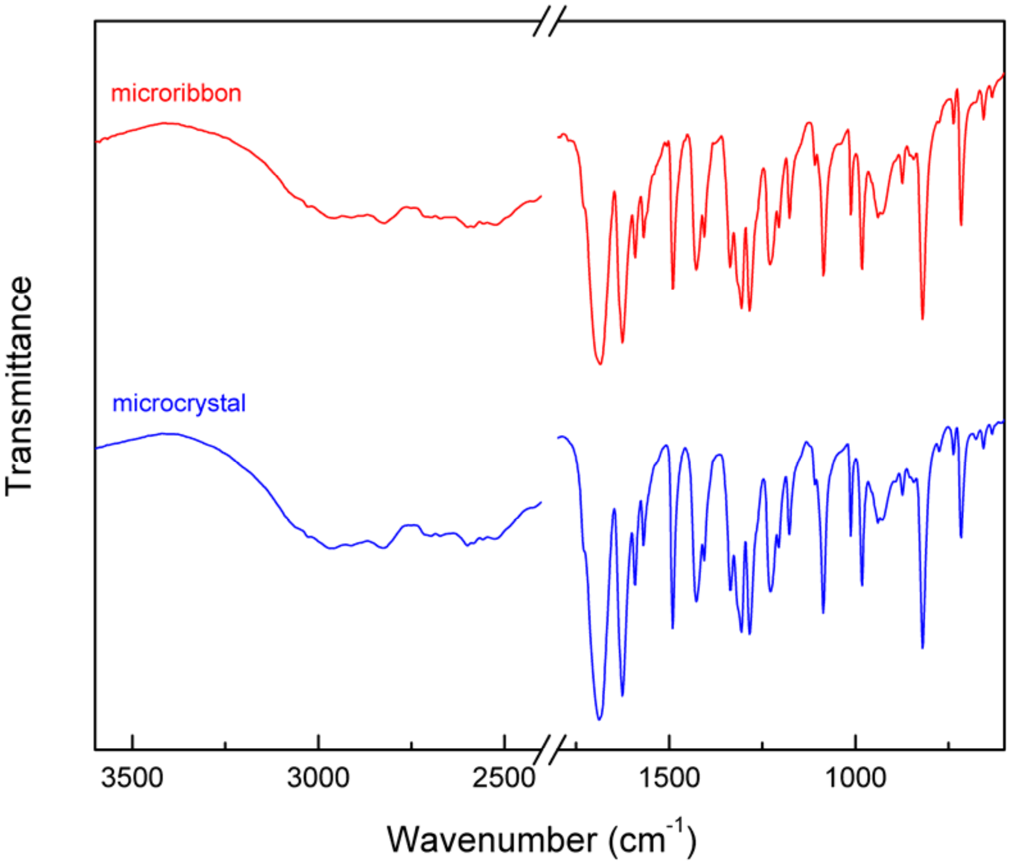

Figure S2. Comparison of infrared spectra of 4Cl-CA microribbon (top, red) and 4Cl-CA microcrystal (bottom, blue). Both samples are exposed under UV for 10 minutes.