

Supplementary information

Ultrafast Photoisomerization of Pinacyanol: Watching an Excited-State Reaction Transiting from Barrier to Barrierless forms

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Evolution associated decay spectra (EADS)

EADS spectra were obtained by global fitting with a $A \rightarrow B \rightarrow C$ sequential model are shown in Fig. S1. The spectrum of A contains the ground state bleaching (GSB) and the stimulated emission (SE) of the S_1 state, with the decay of ~ 100 fs almost independent on the solvent. B also contains the GSB and the SE of the S_1 state; its decay time constant is dependent on the solvent. C represents the difference spectrum between *cis*- and *trans*-isomers and is long-lived.

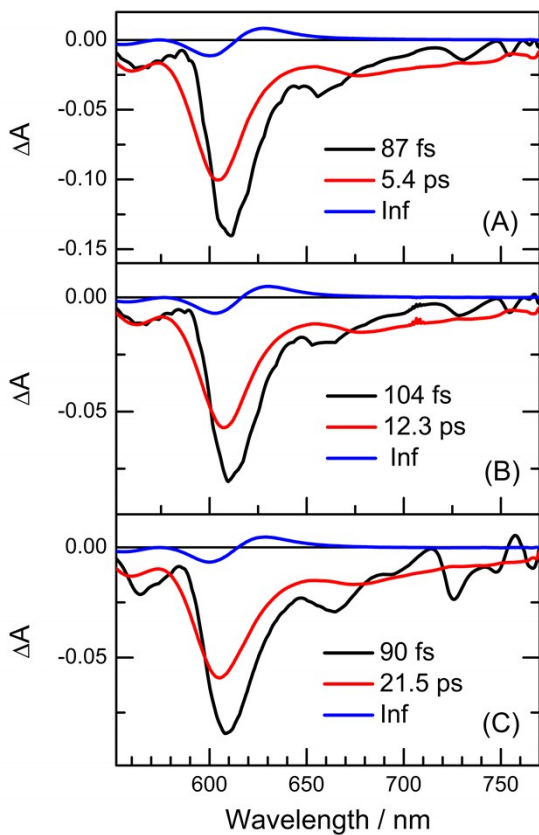


Figure S1. EADS spectra of pinacyanol dissolved in methanol (A), ethanol (B) and propanol (C). Non-smooth behavior of the ~ 100 fs spectra to the red from 700 nm is caused by cross-phase modulation and increased coherent artifacts close to the laser fundamental wavelength, 775 nm.

SE in ethanol and propanol

The increasing rise time constants of the SE are more prominent in ethanol and propanol (Fig. S2).

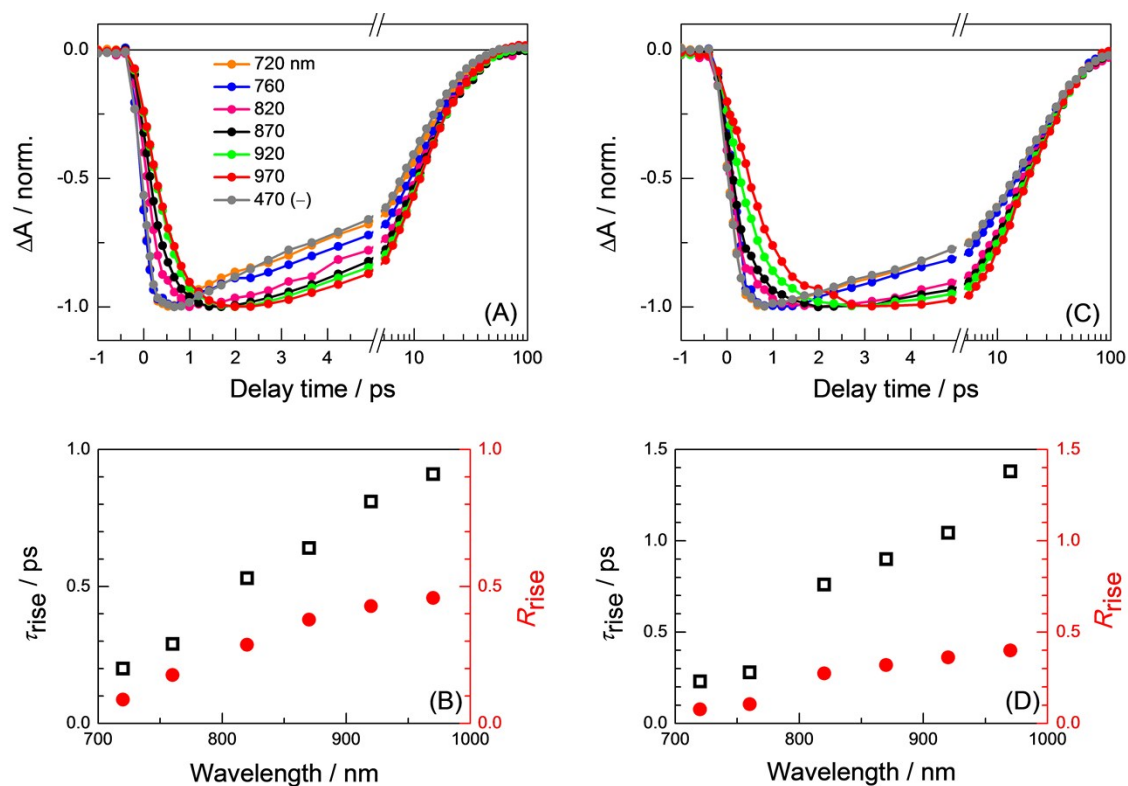


Figure S2. Normalized SE kinetic traces at selected wavelengths and inverted ESA at 470 nm for pinacyanol in ethanol (A) and propanol (C). Rise time constants of SE (black open square, left vertical axis) and relative amplitude of the rise component (red closed circle, right axis) as obtained from fitting the kinetics for ethanol (B) and propanol (D).