Supporting Information

Solvent Control of the Intramolecular Proton Transfer: Is 4-Hydroxy-3-(piperidin-1-ylmethyl)-1-naphthaldehyde a proton crane?

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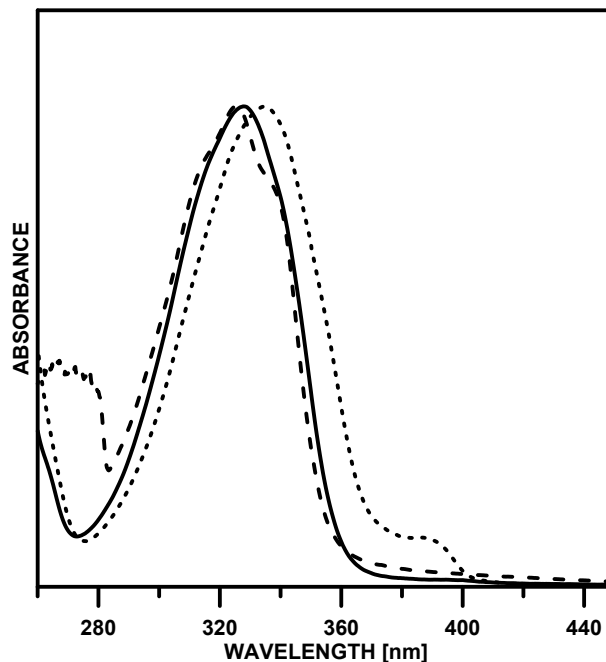[5] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Figure S1. Normalized stationary absorption spectra of **1** in toluene (dashes), acetonitrile (solid line), and methanol (dots).
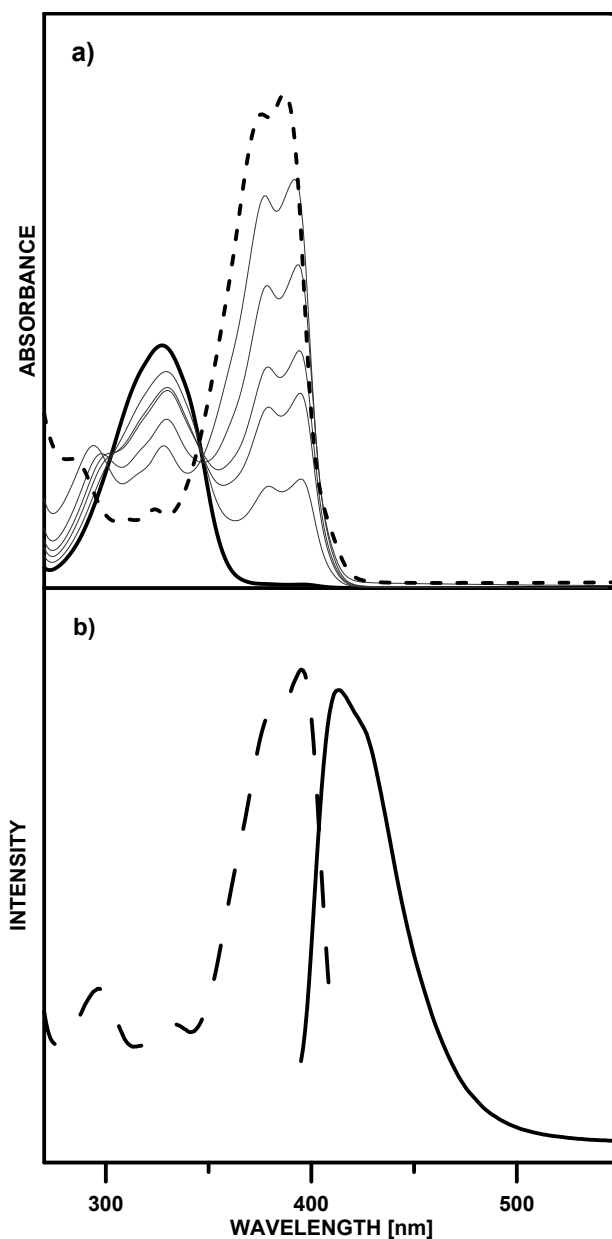
Figure S2. a) Absorption spectrum of **1** upon addition of NH_4OH in acetonitrile: black – without base; grey – gradual addition of base until 1:335 mole ratio **1**:NH_4^+; b) emission spectrum (the same with excitation at 370 and 385 nm), solid line, and excitation (dashes) spectrum upon deprotonation in ACN (corresponds to the dashes above).

Figure S2a) shows the change of the absorption of **1** in acetonitrile upon gradual addition of the base with mole ratios **1**:NH_4^+ of 1:1.86, 1:3.72, 1:5.59, 1:7.46, and 1:18.6 (grey lines).
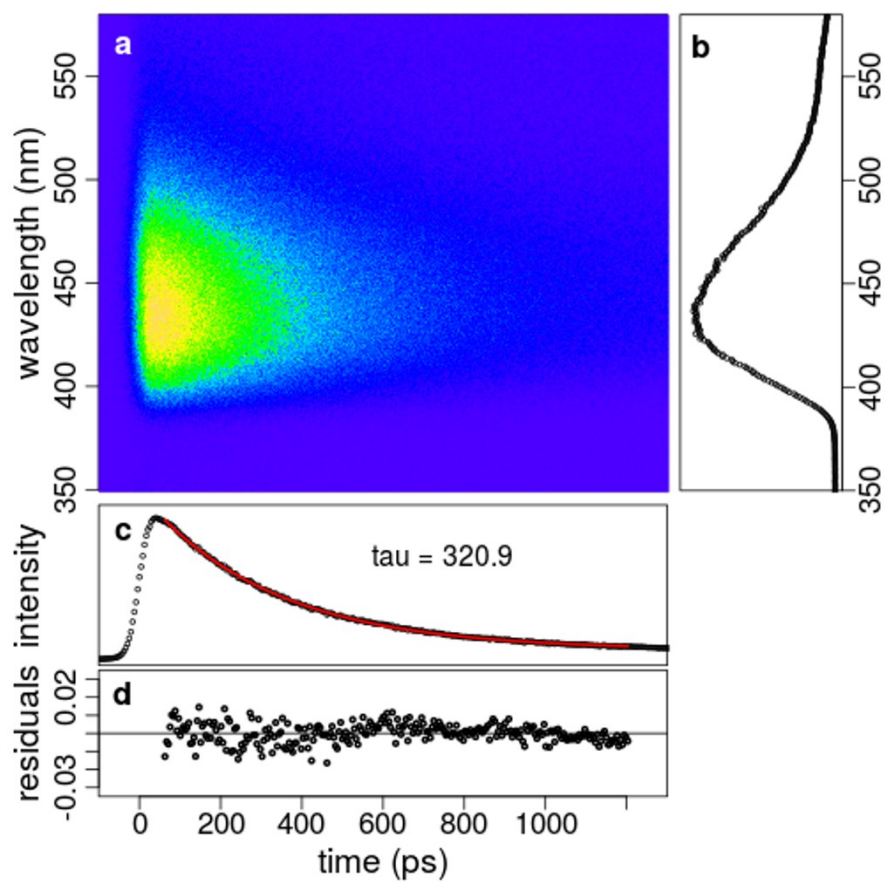
Figure S3. Time resolved fluorescence of **2** in acetonitrile. a) Time- and wavelength-dependent emission intensity of **2** in acetonitrile measured with a streak camera system, b) emission spectra obtained by summation over all times, c) time traces received by the sum over all wavelengths, where the red line shows a mono-exponential fit to the data with a decay time of 320 ps, and d) residual of the fit.
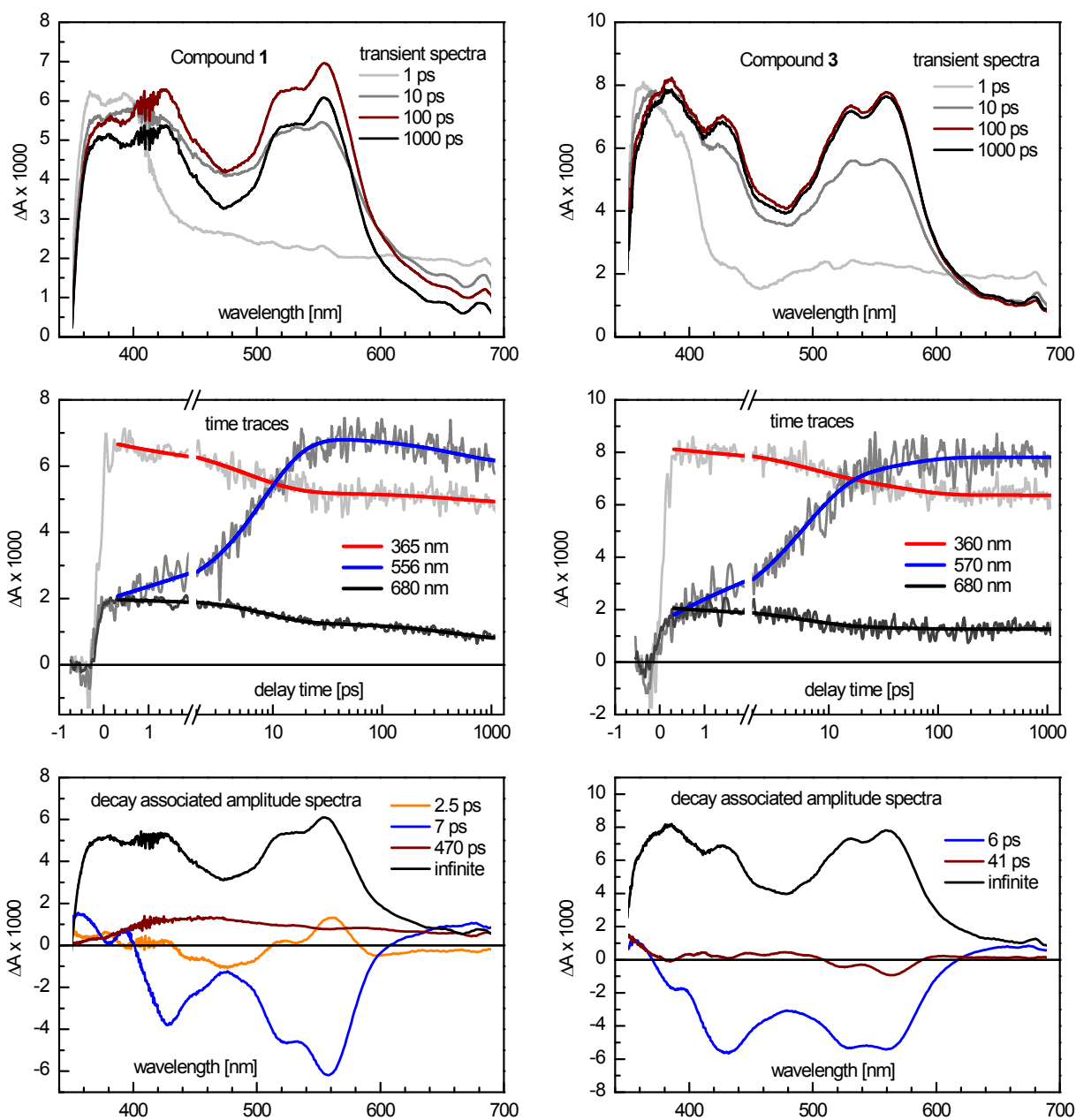
Figure S4. Transient absorption of compounds **1** (left panels) and **3** (right panels) dissolved in probed after excitation 310 nm and probed with magic angle configuration. The upper row shows transient spectra at several delay times, the middle one time traces for selected probe wavelengths and corresponding fit results from a global fit, and the lower row the amplitude spectra of the specified exponential components of the global fit. The dynamics is dominated by a 7 ps respectively 6 ps component which corresponds to a rise of a broad absorption feature with three band maxima at 415 nm, 520 nm, and 560 nm. This long living absorption is assigned to the triplet state in consistency with the observation that both compounds exhibit in acetonitrile no significant fluorescence.
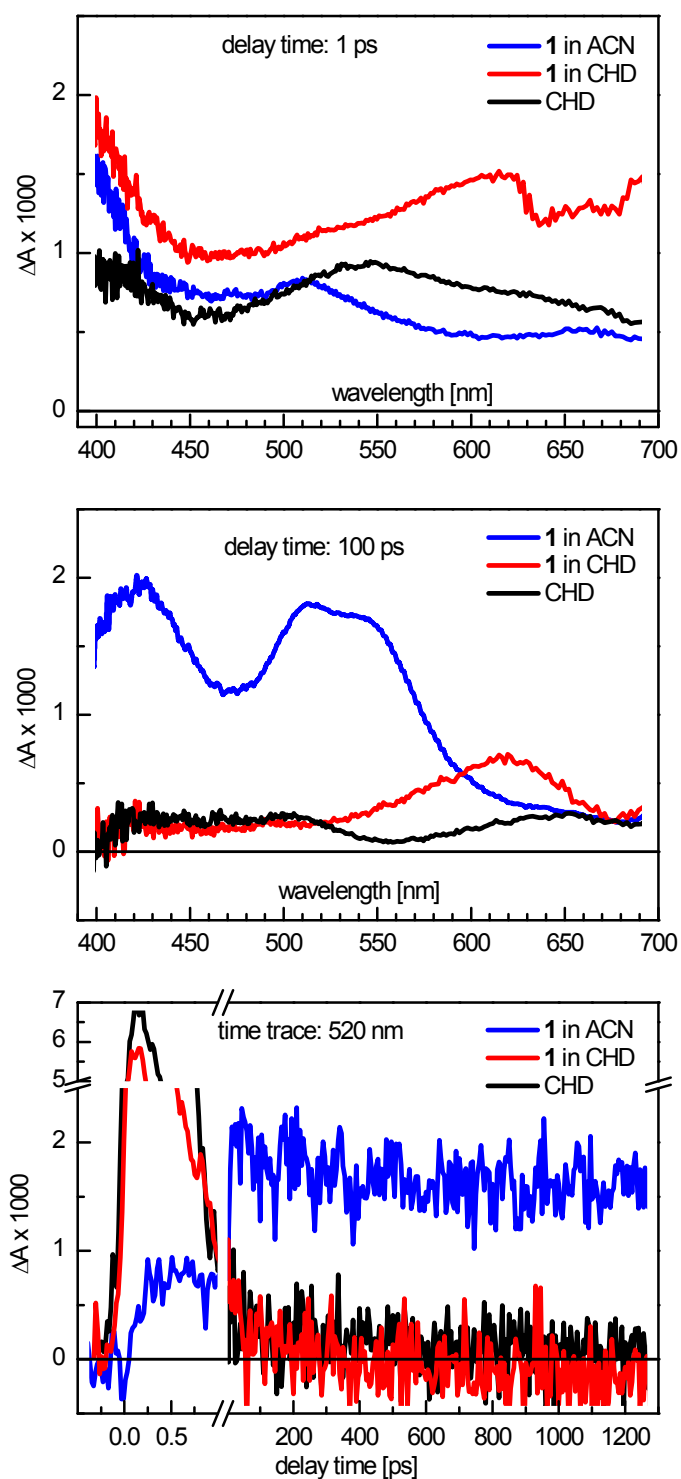
Figure S5.

Transient absorption spectra of **1** in acetonitrile (ACN, blue) and in 1,3-cyclohexadiene (CHD, red) 1 ps (upper panel) and 100 ps (middle panel) after excitation at 337 nm as well as corresponding time traces (lower panel). Measurements in pure CHD are shown for comparison (black curves). The polarizations of pump and probe pulses were perpendicular for technical reasons. In CHD a strong artefact is observed during the first picosecond after the excitation. It is due to the interaction of the pump with the solvent as the experiments in pure CHD demonstrate.

While in ACN a rise of the absorption within 7 ps (confirm Fig. 4S) is observed, the absorption decreases in CHD. As discussed in ref. 24 CHD is a triplet quencher for naphthaldehydes. Since in the case of **1** in CHD no long living absorption is build up we assign the long living absorption observed in other solvents to the triplet state.

2E   TS$_1$ 2PT

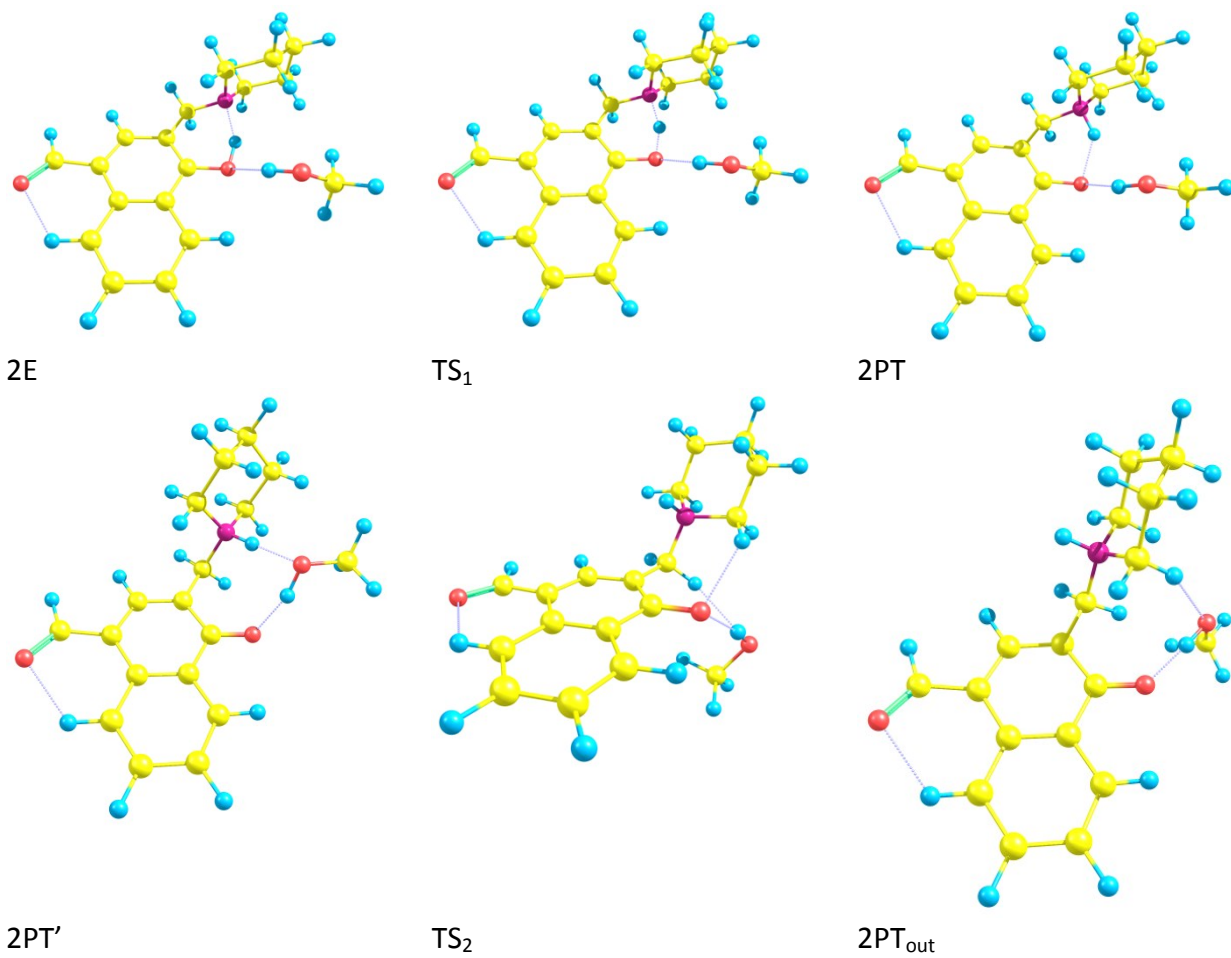2PT'   TS$_2$ 2PT$_{out}$

Figure S6. Ground state structures of the **2**-methanol complexes which are mentioned in Fig. 9.