

Electronic Supplementary Information (ESI) for:

Ultrafast intermolecular proton transfer to a proton
scavenger in an organic solvent

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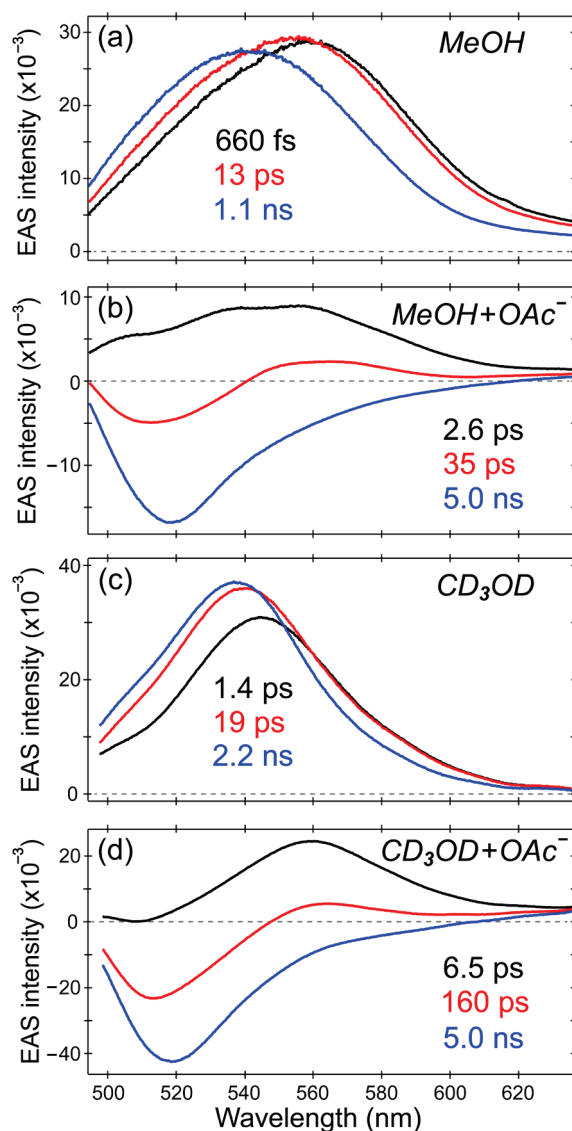


Fig. S1. Time-resolved electronic state evolution of 0.5 mM photoexcited HPTS in methanol with and without 1 M acetate ions following 400 nm photoexcitation. The evolution-associated spectra (EAS) for HPTS in a sequential model from global fitting are shown in (a) MeOH, (b) MeOH+OAc⁻, (c) CD₃OD, and (d) CD₃OD+OAc⁻ with increasing lifetime constants color-coded and listed for the initial spectral component in S₁ (black), intermediate component (red), and the third long component (blue trace) which approaches the fluorescence lifetime. The model includes a ~40 fs Gaussian instrument response function centered at the calculated time zero.

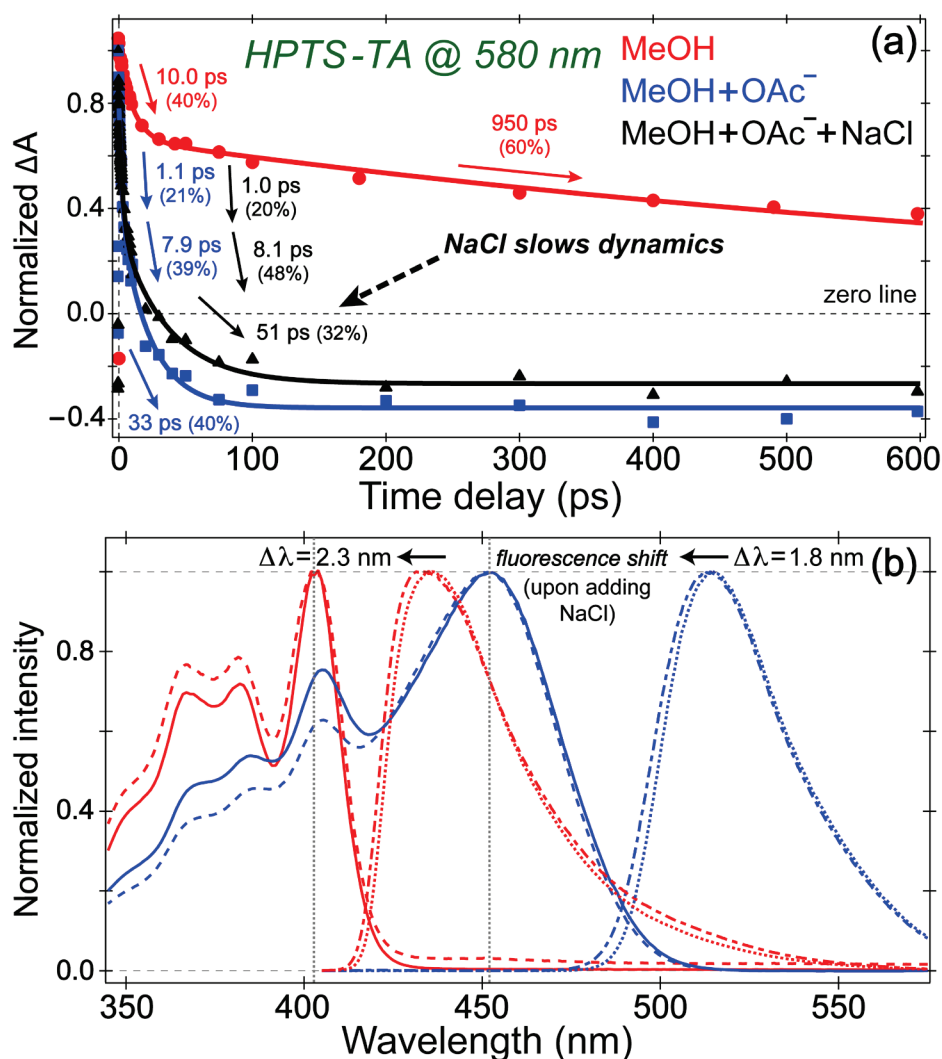


Fig. S2. Effect of inert ions on HPTS transient absorption (TA) and steady-state absorption and emission. (a) TA dynamics monitored at 580 nm for methanol (red circles), methanol-acetate (blue squares), and methanol-acetate-NaCl (black triangles) with least-squares multi-exponential fit as solid traces. Addition of salt to the methanol-acetate solution slows dynamics, particularly for the third dynamic component as pointed by the dashed arrow. (b) The electronic absorption (solid) peak wavelength remains unchanged upon adding NaCl (dashed curve) for HPTS in neat methanol (red) and methanol-acetate (blue), respectively. The vertical dotted lines mark the absorption peak maxima. The emission (dotted) peak exhibits a small but non-negligible blueshift upon adding NaCl (dash-dotted curve) for HPTS in neat methanol (red) and methanol-

acetate (blue), respectively. The horizontal arrows highlight the fluorescence peak blueshift of ~2 nm that is in accord with disruption of the solvation process of HPTS or HPTS-acetate complex by surrounding methanol molecules due to those extra ions from the dissolved salt (i.e., hence a relatively larger energy gap between the emissive state and the electronic ground state).

Notably, the $PA^* \rightarrow PB^*$ conversion enabled by addition of acetate to methanol makes the dynamic plot in (a) convoluted. Therefore, a direct read of the least-squares multi-exponential fit time constants requires caution. The crossover of TA signal taken at 580 nm (see Fig. 2 for the time-dependent plot of the TA spectral traces) from positive to negative at ~25 ps time delay represents the transition from ESA of PA^* to stimulated emission (SE) of PB^* , as a result of the ESPT reaction. The initial two decay components of ~1 ps and 8 ps are likely attributed to the photoexcited molecule moving out of the Franck-Condon region (e.g., coherent proton motions, small-scale skeletal motions)¹⁻³ and initial solvation (e.g., facilitating the formation of a charge-separated state between proton donor and acceptor).^{4,7} The effect of added inert ions on the third decay component is clearly a retardation of ESPT in the solvent H-bonding network, and the listed time constants are derived from least-squares fit of the overlapped signal of exponentially decreasing ESA and increasing SE contributions with opposite signs. The notable increase of the buildup time from ~30→50 ps of PB^* SE (electronic) feature with added salt is also corroborated by the excited-state Raman (vibrational) mode intensity (Figs. 5 and 6) and frequency (Fig. 7) dynamics of HPTS in methanol-acetate following 400 nm photoexcitation.

In comparison, HPTS in neat methanol exhibits a double-exponential decay in TA dynamics (see red trace and the least-squares fit in Fig. S2a). The first ~10 ps component correlates well with the longitudinal relaxation time of methanol molecules, responsible for main solvation events around the HPTS chromophore.⁴ The second long time constant of ~950 ps is

largely reflected by the TA positive ESA signal not dropping to zero after 600 ps (our detection time window) so the molecular system approaches the emissive/fluorescent state of PA* after further solvation and rearrangement of the methanol H-bonding network in the electronic excited state. A tri-exponential fit of the TA kinetic plot at 580 nm yields three time constants: ~535 fs (5%), 11.1 ps (35%), and 970 ps (60%) with fitted amplitude weight percentages noted in parentheses. It is notable that the residual chi square value drops from 3.8×10^{-6} to 2.5×10^{-6} but the additional sub-ps component has a very small weight (i.e., 5% of the total decay).

The TA data can be further analyzed using global analysis.⁸ For example, Fig. S1 above shows the evolution-associated spectra (EAS) of HPTS in CH₃OH and CD₃OD with and without 1 M acetate, reporting on transient electronic states as a function of time delay after fs 400 nm photoexcitation. It is interesting to note that the EAS for HPTS in neat methanol show similar lifetimes of transient species based on a sequential model: ~660 fs, 13 ps, and 1.1 ns (see Fig. S1a) which support the validity of retrieving useful time constants from a relatively clean TA spectral region by directly plotting a slice or region of the TA spectrum and fitting it. For HPTS in neat methanol with one dominant ESA band between ca. 500 and 620 nm, a kinetic analysis at 580 nm (the Raman pump wavelength in this work, see Experimental in main text) provides relevant information about the main HPTS solvation events as corroborated by global analysis. The corresponding ESA results as a function of acetate concentration in methanol are quoted in the main text, which exhibit ~2.2 ps, 50 ps, and 5 ns with 0.75 M acetate and ~1.9 ps, 30 ps, and 5 ns with 1.25 M acetate. The relatively small concentration range is chosen to better compare with the 1 M acetate results, because a certain threshold of base concentration is required for ESPT from HPTS in an organic solvent such as methanol and a quantitative comparison needs to involve similar driving force and activation energy for proton transfer from PA* to acetate.

ESI Table

Table S1. Ground-state Raman peak assignments for HPTS in neat methanol and methanol-acetate solution aided by Gaussian calculations

Exp. freq. ^a (cm ⁻¹)	Cal. freq. ^b (cm ⁻¹)	Vibrational mode assignment (major atomic motions)
171 / 174	178 / 185, 181	Intermolecular H-bond stretch, O···O stretch
239	245 / 250, 246	Ring translation relative to solvent molecule, ring small-scale breathing and bend, and SO ₃ ⁻ sidechain motion
302	318 / 297, 290	Ring translation relative to nearby solvent and/or acetate molecules with some methanol and acetate motions ^c
428 / 432	435 / 431, 442 ^d	Four-ring in-plane deformation with breathing motion ^c
460 / 465	469 / 475, 480 ^e	Four-ring out-of-plane deformation with SO ₃ ⁻ sidechain scissoring motion
663	651 / 654, 652	Four-ring in-plane symmetric stretch
817	836 / 819, 815	Four-ring in-plane asymmetric deformation
954	945 / 953, 936	Out-of-phase HOOP ^f on the HPTS ring system
1300 ^g	1308, 1304 ^g	Four-ring asymmetric breathing with ring-H scissoring
1508 ^g	1512, 1508 ^g	Ring asymmetric C=C stretch with some C–O···H rocking
1594/1587	1598/1589, 1583	HPTS four-ring asymmetric C=C stretch and COH rocking (small, distant proton motion for deprotonated chromophore)
1633/1630 ^h	1635/1634, 1629 ^h	HPTS ring symmetric C=C stretch with large COH rocking (no COH motion for the deprotonated chromophore)

^a Experimentally observed ground state (S₀) Raman mode frequencies from FSRS (Fig. 1b) with the 580 nm Raman pump. The numbers before and after “/” represent the vibrational mode frequencies in methanol and methanol-acetate solution, respectively.

^b The S₀ normal mode frequencies are calculated from *Gaussian* density functional theory (DFT) calculations⁹ of an optimized protonated HPTS chromophore using RB3LYP 6-311G(d,p) or 6-31G(d,p) basis sets in methanol with the default SCRF method IEFPCM (Polarizable Continuum Model using Integral Equation Formalism variant, solvent=methanol). All calculated vibrational frequencies for Raman peaks are scaled with a factor of 0.985 [0.98 for 6-31G(d,p) basis sets

results]. To capture the essence of first solvation shell around the chromophore particularly adjacent to potential deprotonation site, five methanol molecules are positioned near the hydroxyl end (within H-bonding distance, one in the chromophore four-ring plane, two above, and two below) and treated quantum mechanically. The chromophore maintains its four-ring coplanarity after energy minimization in S_0 . Corresponding calculations are also performed at the same level on the largely protonated (i.e., partially deprotonated) and deprotonated chromophore with one acetate acid and four methanol molecules close to the phenolate end. Converged calculation results show that in the former and latter case, the $O\cdots H$ distance in the HPTS hydroxyl moiety is ~ 1.074 and 1.547 Å, the $H^+\cdots OOCCH_3$ distance is 1.390 and 1.025 Å, and the intermolecular $O\cdots H\cdots O$ angle is 171.5° and 172.3° , respectively. These results are listed in this column after “/”, separated by a comma.

^c This motion significantly modulates the distance and angle between the chromophore hydroxyl oxygen with the proton, and one of the acetate oxygen atoms in proximity. We did not perform TD-DFT calculations because the observed vibrational modes start from the Franck-Condon region wherein accurate modeling of non-equilibrium Raman signal evolution is unavailable.^{10,11}

^d Average frequency of two adjacent normal modes with similar in-plane ring deformations.

^e Average frequency of two adjacent normal modes with similar out-of-plane ring deformations. The trend of calculated mode blueshift with increased degree of deprotonation (e.g., $431 \rightarrow 442$, $475 \rightarrow 480$ cm^{-1}) is consistent with the observed mode blueshift and intensity rise in this region.

^f HOOP: hydrogen out-of-plane motion.^{6,12,13} Average frequency of two nearby ring HOOP modes is reported (i.e., each mode involves two adjacent ring-H out-of-phase OOP motions).

^g These vibrational marker bands are associated with the deprotonated chromophore. The calculated normal mode shows significantly enhanced Raman intensity in the deprotonated state *versus* the protonated state of HPTS, wherein for example, a lower frequency mode appears redder at ~ 1295 cm^{-1} that also involves some chromophore COH rocking motions.

^h Upon chromophore deprotonation, a shoulder peak appears at the lower-frequency side of the 1630 cm^{-1} mode in methanol-acetate solution (see Fig. 1b). Calculation for the deprotonated chromophore solvated by an adjacent acetic acid molecule and four methanol molecules shows a 1616 cm^{-1} mode, representing a 13 cm^{-1} redshift from the main calculated peak at 1629 cm^{-1} . This trend supports the observed red shoulder peak down by 12 cm^{-1} (i.e., 1618 vs. 1630 cm^{-1}).

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Full Authorship of Reference 47 in Main Text and Reference 9 in the ESI

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