Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Excited State Structural Dynamics of 4-Cyano-4′-hydroxystilbene: Deciphering the Signatures of Proton-Coupled Electron Transfer using Ultrafast Raman Loss Spectroscopy

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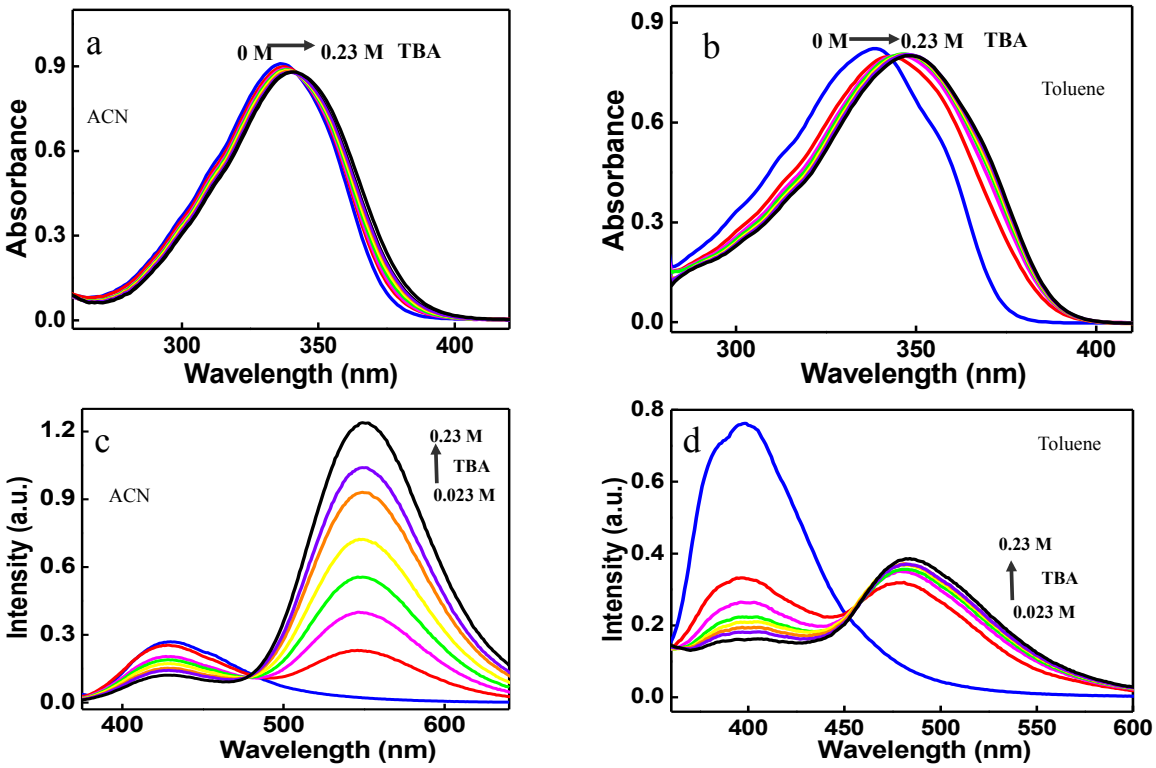

Figure S1: Steady-state absorption (a-b) and emission (c-d) spectra of CHSB in ACN and toluene for different concentrations of TBA. Emission spectra in (c) and (d) are recorded by exciting at 340 nm and 320 nm, respectively.

The absorption maximum of CHSB in ACN is found to shift from ~330 to ~345 nm as the concentration of TBA increases from 0.0 M to 0.23 M, similar to the changes that were observed in case of DCM as the solvent. In toluene, the maximum shifts from ~340 nm to ~355 nm. The emission spectrum of CHSB–TBA in ACN shows a dual band centered at ~425 and ~545 nm. It is also clear that the emission spectrum in ACN is slightly red-shifted when compared to the spectrum in DCM. Such shift may arise due to a better stabilization of the excited polar species by ACN when compared to the moderately polar solvent, DCM. In case of toluene, the emission spectrum shows a dual band centered at ~400 nm and ~490 nm, indicating clearly blue-shifted peaks when compared to DCM. This indicates that the excited states of polar species are relatively less stabilized when compared to DCM.

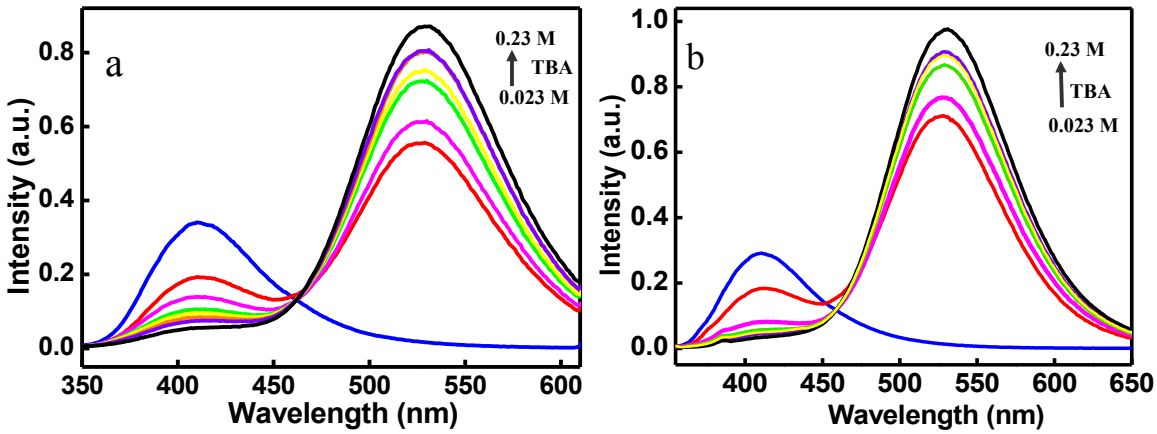

Figure S2: Emission spectra of CHSB in DCM for different concentrations of TBA while exciting at (a) 310 nm and (b) 345 nm.

Figure S2 represents the emission spectra of CHSB in DCM for different concentrations of TBA for excitations at 310 nm and 345 nm, respectively. It is evident from the figures that the emission spectrum exhibits a growth in the dual band structure centered at ~410

and 530 nm with increase in the concentration of TBA. It is also noticed from the figures that different excitations essentially populate the same species in the excited state, therefore exhibiting similar spectral features.

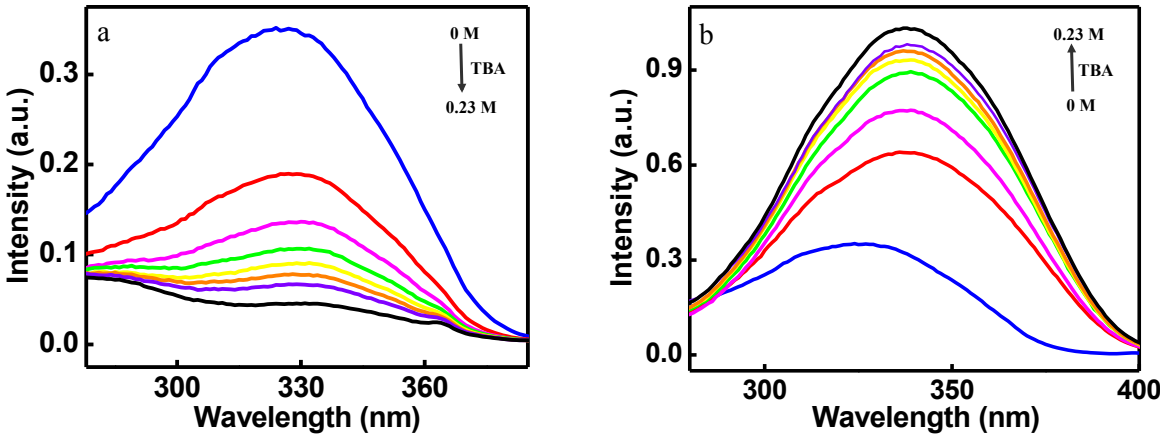

Figure S3: Excitation spectra of CHSB in DCM for different concentrations of TBA for emission monitored at (a) 410 nm and (b) 530 nm. Blue trace in (b) is obtained for the 410 nm emission for CHSB alone and is included for reference purpose.

It is clear from Figure S3(a) that the emission at ~410 nm essentially originates from the absorption band centered around ~330 nm. We can also notice that the intensity of the ~330 nm band gradually decreases as the concentration of TBA increases from 0.0 M to 0.23 M, indicating the suppression of the responsible species for such emission. Similarly, we can notice from Figure S3(b) that the emission at ~530 nm is originating predominantly from the band centered at ~345 nm, whose intensity exhibits a growth with increase in the concentration of TBA, contrary to the case of ~410 nm emission. These features demonstrate that the dual band emission from CHSB in presence of TBA has different origins.

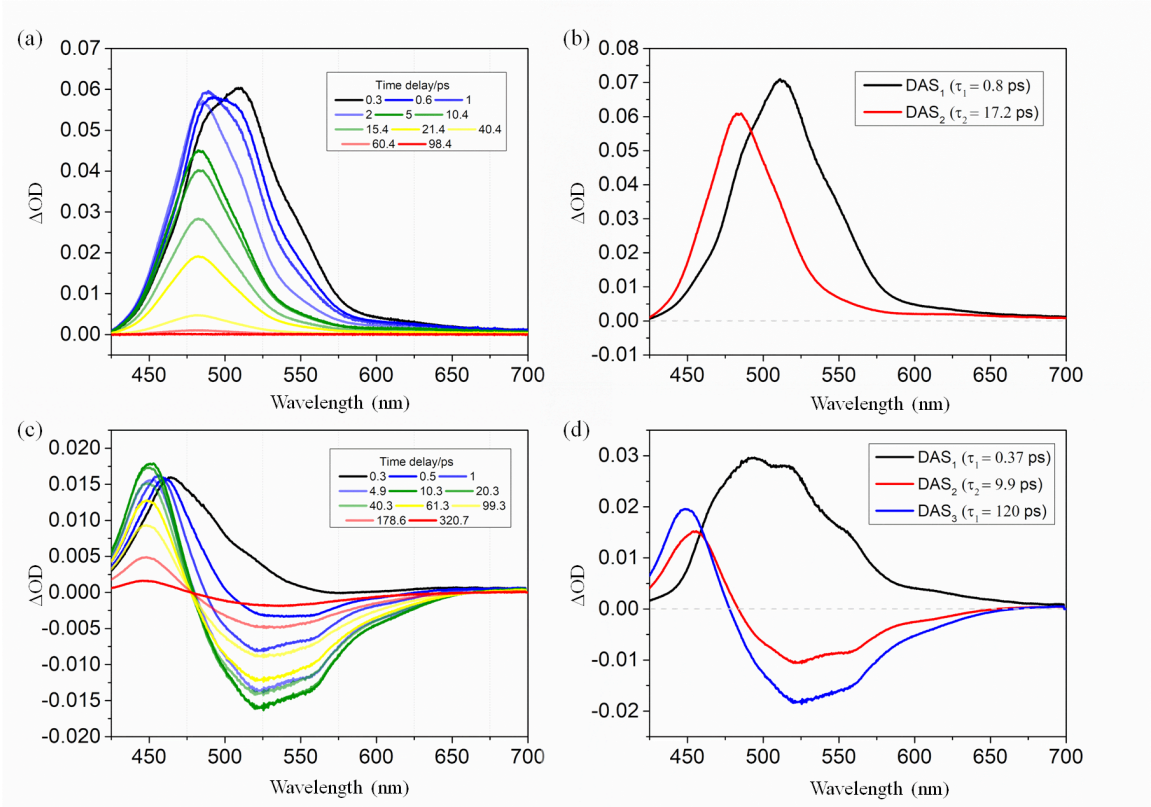

Figure S4: Transient absorption spectra of CHSB in (a) DCM (c) DCM+TBA at different delay time points while exciting at ~350 nm. Decay-associated spectra (DAS) of CHSB in (b) DCM and (d) DCM+TBA.

The transient absorption spectra of CHSB while exciting at ~350 nm in presence and absence of TBA in DCM are given in Figure S6. The spectral features and the DAS as given in Figures S4 (a) and (b) for the CHSB alone are similar to the features as observed for the excitation at ~335 nm. In case of CHSB–TBA, the ESA band appears to be centered at ~450 nm which is blue-shifted as compared to the ~480 nm band for the ~335 excitation, though the stimulated emission band appears to match well in both the cases. We also performed TA measurements while exciting at ~370 nm and noticed that spectral

features are not affected in case of CHSB alone, while a clear shift in the absorption maximum to ~450 nm is observed in case of CHSB–TBA.

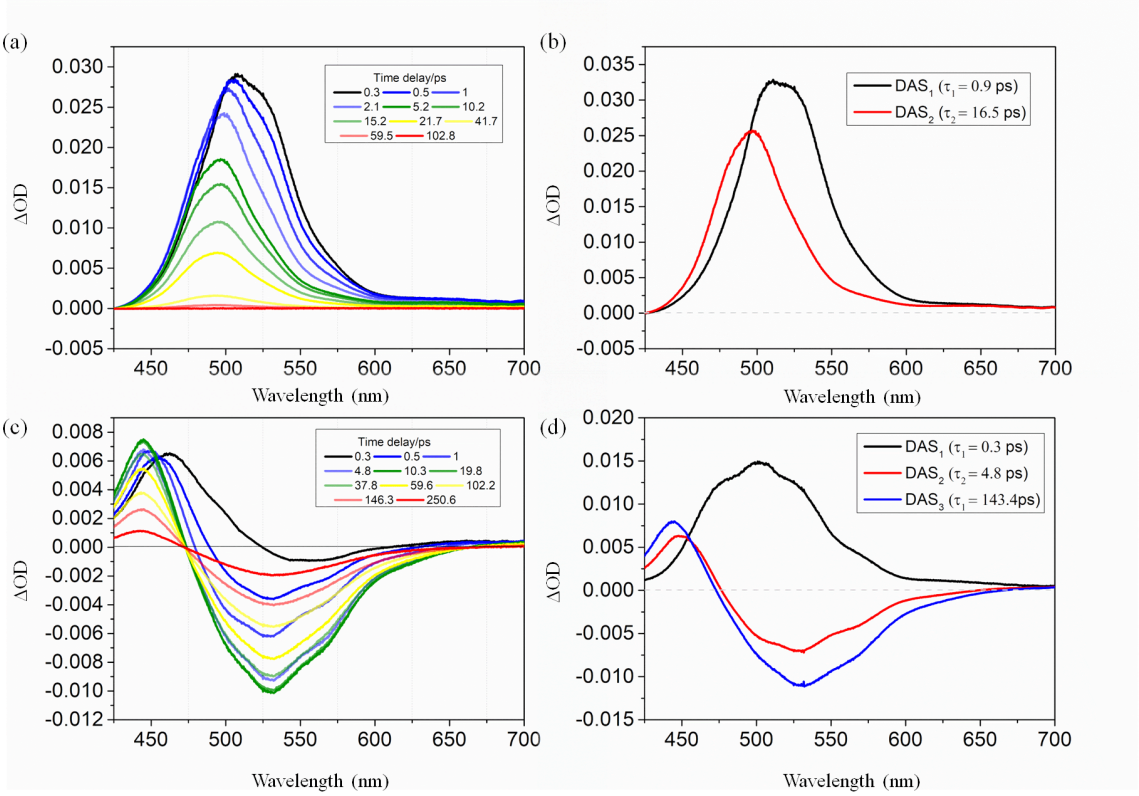

Figure S5: Transient absorption spectra of CHSB in (a) DCM (c) DCM+TBA at different delay time points while exciting at ~370 nm. Decay-associated spectra (DAS) of CHSB in (b) DCM and (d) DCM+TBA.

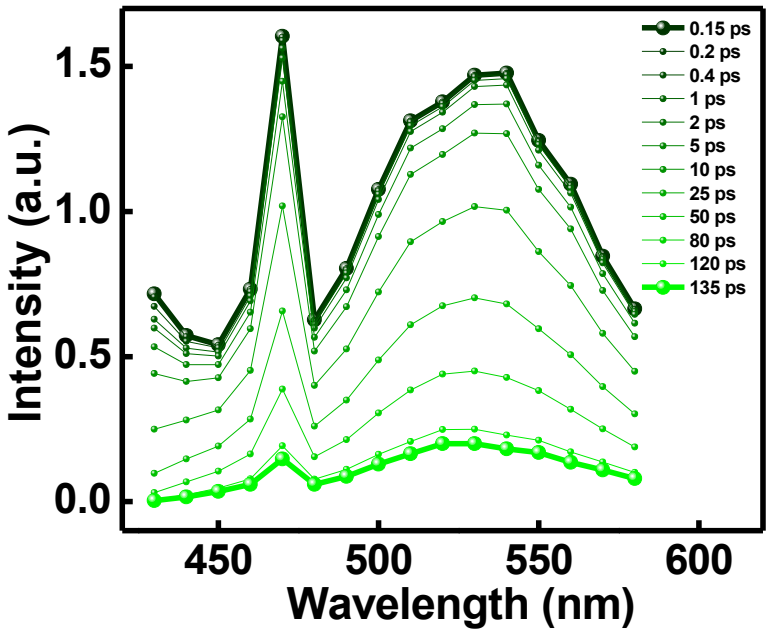

Figure S6: Reconstructed fluorescence spectra at different time points obtained from the fluorescence up-conversion kinetics.

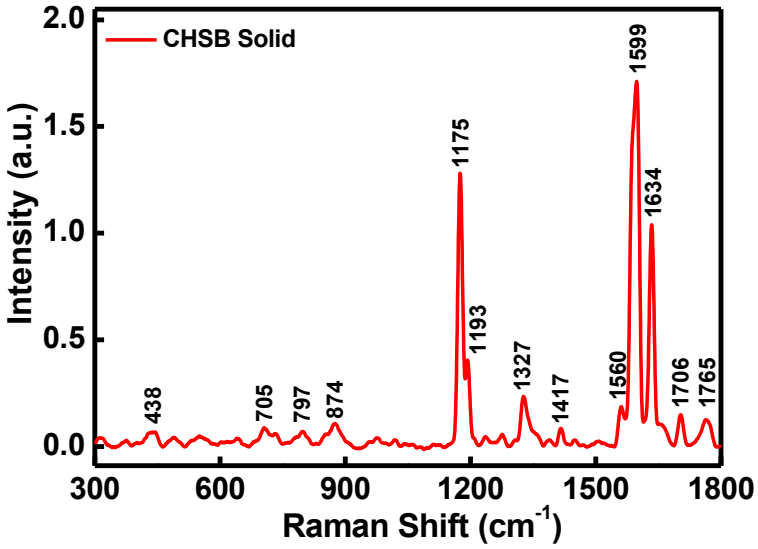

Figure S7: Steady-state Raman spectrum of CHSB in the powdered form recorded using LabRAM confocal Raman spectrometer by exciting at 633 nm.

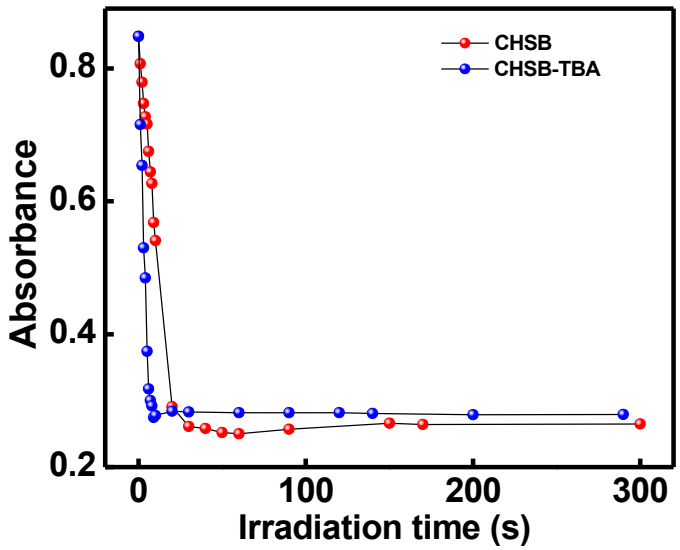

Figure S8: Time-dependent absorbance of CHSB and CHSB–TBA upon UV irradiation in DCM.

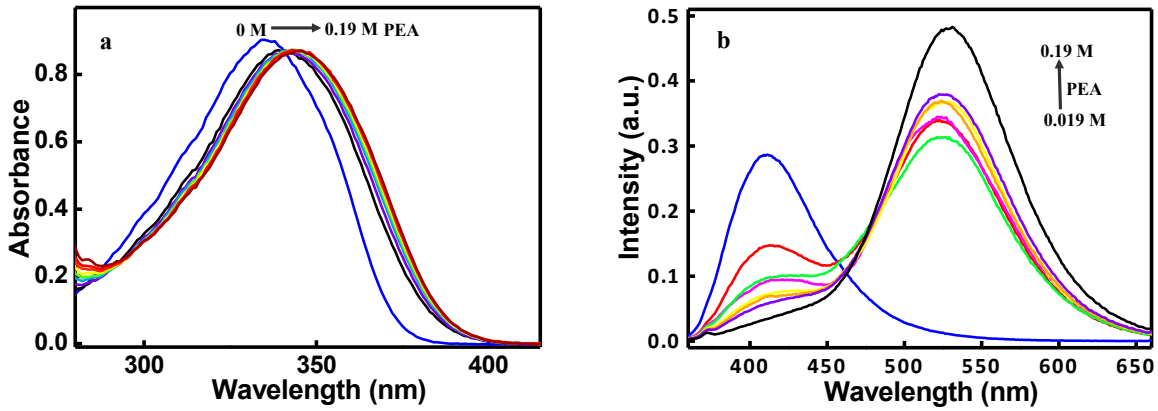

Figure S9: Steady-state absorption (a) and emission (b) spectra of CHSB in DCM for different concentrations of phenylethylamine (PEA). Emission spectra are recorded by exciting at 370 nm.

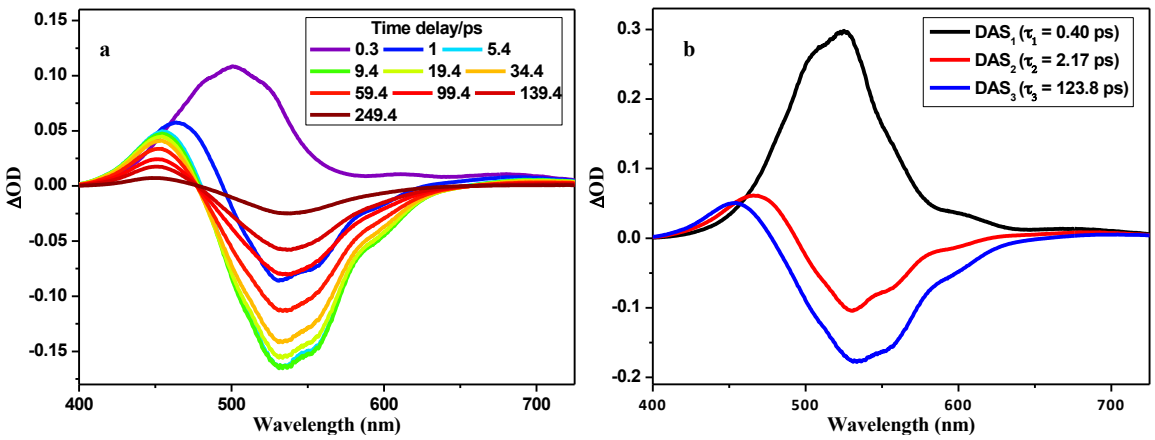

Figure S10: (a) Transient absorption spectra at different delay time points and (b) decay-associated spectra of CHSB in phenylethylamine (PEA) while exciting at ~370 nm.

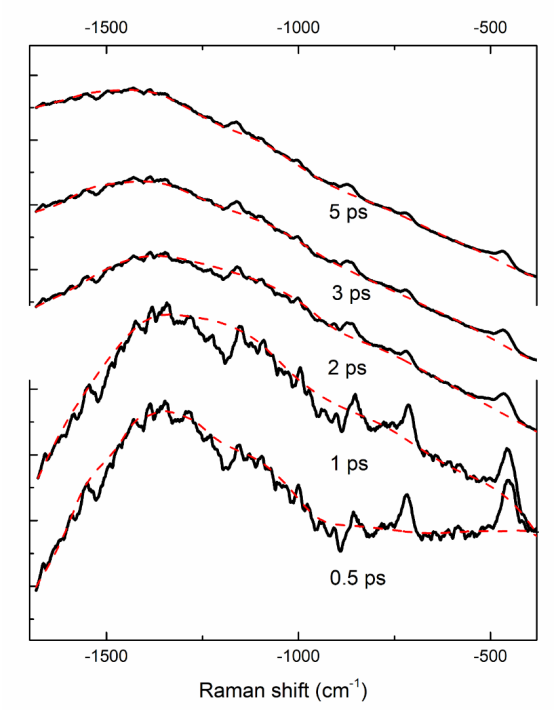

Figure S11: Raw URL spectra (black) with baselines (red) for selected time delays for CHSB with TBA.

Table S1: Kinetic parameters of the Raman amplitudes for CHSB in absence and presence of TBA. Amplitude weightages for each time constant are given in the parentheses. The rise time constants are given in blue fonts.

Raman modes (cm^{-1})	**CHSB**		Raman modes (cm^{-1})	**CHSB-TBA**		
	τ_1 (ps)	τ_2 (ps)		τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
1523	0.90 ± 0.07 (75)	10.20 ± 2.1 (25)	**1584**	0.50 ± 0.10 (12)	8.30 ± 1.30 (34)	84.20 ± 4.00 (54)
1494	0.80 ± 0.10 (83)	8.30 ± 1.40 (17)	**1565**	0.45 ± 0.08 (14)	10.90 ± 2.20 (30)	78.50 ± 7.00 (56)
1326	0.90 ± 0.12 (81)	11.20 ± 1.70 (19)	**1174**	0.30 ± 0.10 (10)	7.20 ± 1.80 (36)	83.20 ± 5.00 (54)
448	1.10 ± 0.08 (78)	9.80 ± 1.40 (22)	**854**	0.46 ± 0.11 (16)	8.60 ± 2.00 (42)	90.20 ± 7.00 (42)