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Coupled Electron and Proton Transfer Processes in 4-Dimethylamino-2-hydroxy-benzaldehyde

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ABSTRACT: TDDFT calculations, picosecond transient absorption, and time-resolved fluorescence studies of 4-dimethylamino-2-hydroxy-benzaldehyde (DMAHBA) have been carried out to study the electron and proton transfer processes in polar (acetonitrile) and nonpolar (*n*-hexane) solvents. In *n*-hexane, the transient absorption (TA) as well as the fluorescence originate from the $\pi\pi^*$ state of the keto form (with the carbonyl group in the benzaldehyde ring), which is produced by an intramolecular proton transfer from the initially excited $\pi\pi^*$ state of the enol form (OH group in the ring). The decay rate of TA and fluorescence are essentially identical in *n*-hexane. In acetonitrile, on the other hand, the TA exhibits features that can be assigned to the highly polar twisted intramolecular charge transfer (TICT) states of enol forms, as evidenced by the similarity of the absorption to the TICT-state absorption spectra of the closely related 4-dimethylaminobenzaldehyde (DMABA). As expected, the decay rate of the TICT-state of DMAHBA is different from the fluorescence lifetime of the $\pi\pi^*$ state of the keto form. The occurrence of the proton and electron transfers in acetonitrile is in good agreement with the predictions of the TDDFT calculations. The very short-lived (~ 1 ps) fluorescence from the $\pi\pi^*$ state of the enol form has been observed at about 380 nm in *n*-hexane and at about 400 nm in acetonitrile.

1. INTRODUCTION

Proton-coupled electron transfer (PCET) in an electronically excited state plays a crucial role in a wide range of chemical and biological processes, including the conversion of energy in photosynthesis and respiration.^{1–8} Most of the excited-state intramolecular PCET reactions have been studied for molecules that have bifunctional groups in which the excited-state proton transfer induces an intramolecular electron transfer.

4-Dimethylamino-2-hydroxy-benzaldehyde (DMAHBA), Scheme 1, is a very good example of a PCET molecule, which contains orthohydroxybenzaldehyde^{9–11} capable of excited-state intramolecular proton transfer (ESIPT) and 4-dimethylaminobenzaldehyde (DMABA) that exhibits intramolecular charge transfer in polar solvents.^{12–14} From the detailed study of absorption and fluorescence, Mahanta et al.¹⁵ proposed that DMAHBA exhibits coupled proton and electron transfer in polar solvents and only the excited-state proton transfer in nonpolar solvents. As in DMABA,^{13,16} the electron transfer in the polar solvents of DMAHBA may be assumed to involve the formation of the twisted intramolecular charge transfer (TICT) state^{17,18} in which the positively charged dimethylamino group is twisted with respect to the plane of the negatively charged orthohydroxybenzaldehyde moiety.

To characterize the electronic state and reaction pathways leading to the proton coupled electron transfer, it is essential to carry out the quantum chemistry calculations of geometries,

Scheme 1

energies, and reaction pathways and to compare them with time-resolved fluorescence and transient absorption studies. In this paper, we present a concerted experimental and computational study of PCET in DMAHBA.

2. EXPERIMENTAL AND CALCULATIONS SECTION

A sample compound of DMAHBA was synthesized as described in ref 15 and purified by column chromatography. The steady-state UV absorption and fluorescence spectra were measured by using a UV spectrophotometer (Shimadzu, UV-1800) and a spectrofluorometer (Horiba/Jobin Yvon, FluoroMax-4),

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Figure 1. Schematic diagram for the time-resolved fluorescence spectra measurement using Kerr gating technique: F1 is a sharp cutoff filter to eliminate the excitation laser wavelength; F2 is a notched filter to cut the switching pulse interference; PM denotes an off-axis parabolic mirror; P1 is a thin polarizer; L is a collimating lens (see text for more details).

respectively. Spectral corrections for the fluorescence spectra were made for correct spectral profile.

The time-resolved excited-state absorption spectra were measured using the Ti:Sapphire-based transient absorption setup described in refs 16 and 19. Briefly, the subpicosecond pump–probe experiments were carried out using ~ 100 fs pump pulses with a center wavelength of 315 nm from an optical parametric amplifier (Light Conversion, TOPAS), which was pumped by the fundamental (800 nm) of the Ti:Sapphire regenerative amplifier (Quantronix, Titan). A weak fundamental beam of the regenerative amplifier traveling through a variable delay stage was focused onto a CaF_2 plate to generate a probe white light continuum (320–750 nm). The probe pulse was then focused to the sample solution in a flow cell (1.0 mm thickness) and intersected the pump beam with a narrow crossed angle ($< 5^\circ$). We installed a linear motion of the cell implemented via a crank mechanism to make its surfaces periodically changed during irradiation of the UV-pump beam. It helped to prevent photopolymerized sample adsorbing onto the inner cell surface, especially in *n*-hexane solution. The time-resolved transient absorption (TA) spectra were mapped out as a function of delay time between the pump and probe pulses, using a CCD detector (Princeton Instruments, PIXIS 400B) attached to a spectrograph (Acton, Spectra Pro 2300i). Temporal decay profiles at specific wavelengths were extracted from the mapped TA spectra and analyzed by deconvolution procedures with nonlinear least-squares fittings. The multiple-exponential fitting function $\sum_i A_i \exp(-t/\tau_i) + A_\infty$ was analytically convoluted with a Gaussian function, whose fwhm was also one of fit parameters to be optimized, to model the instrument response function. A long-live component (nanoseconds) due to the triplet–triplet absorption was treated as the background as A_∞ in the fitting function.

Picosecond time-resolved fluorescence spectrum (TRFS) was obtained by an optical Kerr-gating technique to skim an emission spectrum as a function of the delay time (Figure 1). Benzene as Kerr medium was filled in a static cell (1 mm thickness) and

Table 1. TD/B3LYP Vertical Excitation Energies ΔE (in eV), Oscillator Strength (f), and Orbital Transitions of the Enol Form of DMAHBA

state	ΔE^a	f	transition
$S_1 (n\pi^*)$	4.111	0.0002	H-2 $\rightarrow$ L
$S_2 (\pi\pi^*)$	4.127	0.0671	H-1 $\rightarrow$ L
$S_3 (\pi\pi^*)$	4.197	0.4231	H $\rightarrow$ L
$S_4 (\pi\pi^*)$	5.070	0.0605	H $\rightarrow$ L + 1
$S_5 (\pi\pi^*)$	6.035	0.0769	H-3 $\rightarrow$ L, H-1 $\rightarrow$ L + 1

^a Calculated at B3LYP/cc-pVDZ S_0 geometry.

placed between two thin high-contrast polarizers (Moxtek, ProFlux PFU05C) at crossed polarization configuration. The excitation beam was focused onto the sample in the flow cell and its emission was collected collinearly along the pump beam, and imaged onto the Kerr cell via two parabolic reflectors. The gating pulse (800 nm, $< 100 \mu\text{J}$) was traveling through a variable delay stage (Newport, IMS600CCHA) and focused to the Kerr cell, where the emission and the gate pulse spatially overlapped each other, as well as in time, to drive the Kerr-shutter open at a given delay time. The typical temporal resolution was estimated as ~ 1 ps for the Kerr-gating. Finally, so-obtained gated-fluorescence was introduced to a polygraph spectrometer (Acton, Spectra Pro 2300i) attached to a CCD detector (Princeton Instruments, PIXIS 400B) to create the spectrum. Temporal decay profiles at specific wavelengths were extracted from the mapped spectra and analyzed by deconvolution procedures with nonlinear least-squares fitting.

Fluorescence lifetime measurements were carried out by using the time-correlated singlet-photon counting (TCSPC) technique. The excitation source was a frequency-doubled output of cavity-dumped dye laser (Coherent; 702-1D) pumped by the 527 nm output of a 76 MHz mode-locked Nd:YLF laser (Quantronix, 4217 ML). The fluorescence was collected with a

Figure 2. TD/B3LYP/cc-pVDZ electronic energy profiles of DMAHBA in (a) $n\pi^*$ and $\pi\pi^*$ state along proton transfer path, calculated along the O(ring)H distance; (b) those of the $\pi\pi^*$ state and TICT state of keto form along rotation of the dimethylamino group, as calculated as a function of the CNCC dihedral angle; (c) back proton transfer path in the TICT states, as calculated as a function of the O(ring)H distance. The dipole moments of the excited states are given in Debye.

Table 2. TD/B3LYP/cc-pVDZ Relative Energy of the Different Isomers Associated with PCET in DMAHBA System

states	ΔE^a (kcal/mol)
$n\pi^*/\pi\pi^*$ (enol form)	0
$\pi\pi^*$ (keto form)	−12.1
TICT (keto form)	−17.7
TICT (enol form)	−18.6

^a Relative energy to −554.34722 au for the minimum of $n\pi^*$ state or the maximum of $\pi\pi^*$ state in the enol form.

Table 3. Comparison of TD/B3LYP Vertical Emission Energies ΔE (in nm), Oscillator Strength (f), and Orbital Transitions of the Fluorescent $\pi\pi^*$ States of DMAHBA with Experiment

excited state	ΔE	f	transition	experiment ^a
$\pi\pi^*$ (enol form)	380 nm	0.423	L → H	380 nm
$\pi\pi^*$ (keto form)	523 nm	0.019	L → H	525 nm

^a This work in *n*-hexane.

Table 4. TD/B3LYP/cc-pVDZ Vertical Excitation Energies ΔE (in eV), Oscillator Strengths f of Excited States of DMAHBA

excited states	transitions ^a	ΔE	f
$n\pi^*$ (enol form)	$S_1 \rightarrow S_6$	2.26 (549 nm)	0.055
	$S_1 \rightarrow S_9$	2.67 (464 nm)	0.032
	$S_1 \rightarrow S_{11}$	3.11 (398 nm)	0.125
	$S_1 \rightarrow S_{13}$	3.21 (386 nm)	0.159
$\pi\pi^*$ (keto form)	$S_1 \rightarrow S_9$	2.59 (479 nm)	0.079
	$S_1 \rightarrow S_{13}$	2.91 (426 nm)	0.145
	$S_1 \rightarrow S_{15}$	3.12 (398 nm)	0.061
	$S_1 \rightarrow S_{17}$	3.39 (366 nm)	0.071
	$S_1 \rightarrow S_{20}$	3.73 (333 nm)	0.040
	$S_1 \rightarrow S_4$	2.54 (488 nm)	0.147
	$S_1 \rightarrow S_5$	2.88 (431 nm)	0.418
TICT (keto form)	$S_1 \rightarrow S_6$	5.70 (217 nm)	0.270

^a Only transitions with $f > 0.03$ are listed for the 330–550 nm range. The initial state of the excited-state absorption is designated as S_1 .

Figure 3. Schematics for coupled electron and proton transfer processes in 4-dimethylamino-2-hydroxy-benzaldehyde (DMAHBA) in the polar environment following photoexcitation.

microchannel plate photomultiplier (MCP, Hamamatsu; R3809U-51) through a high-throughput 0.1 m monochromator (JY/SPEX, H10). The output of the MCP was fed to an onboard TCSPC module (Becker and Hickl, SPC-300) as a multichannel analyzer. The temporal response of the detection system was less than

30 ps (fwhm) after deconvolution procedures using nonlinear least-squares fittings.

All experiments were carried out at room temperature.

Figure 4. Comparison of the steady-state absorption and fluorescence spectra of DMAHBA in *n*-hexane (blue) and acetonitrile (red) measured at room temperature. The fluorescence spectra were obtained in the excitation of 300 nm and corrected with respect to spectral response of the instruments used. The fluorescence excitation spectrum (not shown) of the 525 nm emission in *n*-hexane, and that of 545 nm in acetonitrile, corresponds to the respective absorption spectrum of DMAHBA.

The time-dependent DFT (TDDFT) calculations of the excitation energies and oscillator strengths of the excited-state absorptions, as well as the dipole moments of various excited states, were performed using TURBOMOLE suite of programs²⁰ with B3LYP functional and cc-pVDZ basis set. The geometries of the excited S_1 ($n\pi^*$) and S_2 ($\pi\pi^*$) states were optimized at fixed OH distances to follow the proton transfer process in the electronic excited state at the TD/B3LYP level and to obtain the energy barrier for this process. We have also optimized geometries of the S_1 state of the keto tautomer for fixed values of the CN(DMA)CC dihedral angle to find the energy barrier for an electron transfer process, when going from the $\pi\pi^*$ state to the TICT state.

3. RESULTS AND DISCUSSION

3.1. Computational. **3.1.1. Equilibrium Geometry of the Ground (S_0) State and Vertical Excitation Energies.** The ground-state geometries of DMAHBA, optimized at the B3LYP level using the cc-pVDZ basis sets, have been used to calculate the TD/B3LYP vertical excitation energies, oscillator strengths, and orbital transitions of the enol form. As expected, the ground electronic (S_0) state is stabilized in the closed enol form (Scheme 1) by strong intramolecular hydrogen bond between the hydrogen of the hydroxyl ($-\text{OH}$) group and the oxygen of the aldehyde ($-\text{CHO}$) group. The S_0 state of the keto form is unstable and gives into the enol form in the TDDFT calculations.

Figure 5. Picosecond time-resolved fluorescence spectra (TRFS) and their temporal characteristics of DMAHBA in *n*-hexane at room temperature for short time (a, b) and long time (c, d) ranges. TRFS were obtained by Kerr-gating techniques, and the temporal profiles were extracted with the band-integration of emission at its center wavelength in the TRFS. Leaders show the fit decay times (see Table 5 for details). Note that a short-lived fluorescence from the initially excited $\pi\pi^*$ state of enol form is detected at 380 nm as the spiky feature (fwhm ~ 1.1 ps). The system response time of 600 fs (fwhm) is obtained from solvent Raman signal. The decay time constants were evaluated by a nonlinear least-squares fit with deconvolution procedure.

Figure 6. Picosecond time-resolved fluorescence spectra (TRFS) and their temporal characteristics of DMAHBA in acetonitrile at room temperature for short time (a, b) and long time (c, d) ranges. TRFS were obtained by Kerr-gating techniques, and the temporal profiles were extracted with the band-integration of emission at its center wavelength in the TRFS. Leaders show the fit decay times (see Table 5 for details).

Table 1 presents the TD/B3LYP vertical excitation energies and oscillator strengths of the enol form of S_0 DMAHBA. The results indicate that there are three low-lying excited states of very similar energies: an $n\pi^*$ and the two low-lying $\pi\pi^*$ states. The transition to the $^1n\pi^*$ state (characterized by the excitation from the lone-pair of the carbonyl oxygen atom) is extremely weak (oscillator strength: $f \sim 0.0002$), whereas the transition to the S_3 ($\pi\pi^*$) state is much stronger. The excitation energy and oscillator strength of the strongly allowed ($f \sim 0.4$) $^1\pi\pi^* \leftarrow S_0$ transition are consistent with the steady-state absorption band of DMAHBA at about 340 nm (molar absorption coefficient: $\epsilon \sim 3.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$).

The S_0 isomer with no internal hydrogen bond (open form; Scheme 1) is calculated as 13.45 kcal/mol above the S_0 isomer with the hydrogen bond (B3LYP). In the non-hydrogen-bonded isomer, the $n\pi^*$ state is well below the lowest $\pi\pi^*$ state. The corresponding energy gaps are 0.7 eV at the S_0 geometry, 0.98 eV at the $n\pi^*$ geometry, and 0.67 eV at the $\pi\pi^*$ geometry.

3.1.2. Vertical Excitation Energies of the Excited Electronic States. The two $\pi\pi^*$ states of the enol form are unstable with respect to the proton transfer, which creates the $\pi\pi^*$ state of the keto form (with the C=O group in the ring). The TD/B3LYP/cc-pVDZ calculation indicates that the $\pi\pi^*$ state of keto form is more stable than the $\pi\pi^*$ state of enol form by about 12.1 kcal/mol, Figure 2a. It is, therefore, expected that the $\pi\pi^*$ state of enol form, formed by the $\pi\pi^* \leftarrow S_0$ excitation, would rapidly produce the $\pi\pi^*$ state of keto form by proton transfer. Table 2 lists the relative stability of the different forms relevant to the PCET of DMAHBA. Table 3 presents the vertical emission energies for the $\pi\pi^*$ states of the enol and keto forms of

DMAHBA. The calculated TD/B3LYP/cc-pVDZ vertical emission energy (the difference between S_1 and S_0 energies at the S_1 minimum) of the $\pi\pi^*$ state of the keto form is 2.37 eV (or 523 nm), with the oscillator strength of emission being 0.019. We identify this with the observed emission at about 525 nm in *n*-hexane (section 3.2). In the enol form, only the $n\pi^*$ state is stable against the proton transfer. The TD/B3LYP energy of enol $n\pi^*$ state is 0.5 eV below the nearly degenerate energies of the two enol $\pi\pi^*$ states.

Our calculations also indicate that there is an energy barrier of about 3 kcal/mol for an electron transfer process that leads the $\pi\pi^*$ state of keto form to a TICT state in which the positively charged dimethylamino group is perpendicular to the negatively charged orthohydroxybenzaldehyde moiety, Figure 2b. The keto form of the TICT state is unstable with respect to a proton transfer that creates the enol form of the TICT state Figure 2c. The energy barrier for the process is rather small (~ 0.5 kcal/mol) and the production of the TICT state of enol form from the TICT state of keto form should be very fast (<100 fs). The radiative transition probability of the enol form of the TICT state is extremely small ($f \sim 1.6 \times 10^{-6}$), so that the state is expected to decay (to the ground and triplet states) by radiationless transition. We also note that the back proton transfer in the TICT state increases slightly the charge separation, changing the permanent dipole moment from 13.31 D in the ketone to 14.52 D in the enol, Figure 2c. Table 4 summarizes the TDDFT vertical transient absorption energies of excited states of DMAHBA, which are pertinent to the experiment. The structural changes that accompany the proton and electron transfers are schematically illustrated in Figure 3.

Figure 7. Temporal characteristics of the fluorescence from the $\pi\pi^*$ state of the keto form of DMAHBA, measured at different emission wavelengths by the time-correlated single-photon counting (TCSPC) following 315 nm excitation. The fluorescence decay curves are plotted (dots), together with the nonlinear least-squares fits (blue) and the instrument response functions (red). The fit decay times with a standard deviation in the parentheses are shown (see details in Table S).

3.2. Experimental Section. **3.2.1. Steady-State Absorption and Fluorescence.** The steady-state absorption and corrected fluorescence spectra of DMAHBA in *n*-hexane and acetonitrile, at room temperature, are shown in Figure 4. The intensity maxima of the fluorescence spectra lie at 545 nm in acetonitrile and 525 nm in *n*-hexane. The strong absorption ($\epsilon \approx 3.0 \times 10^4$ l mol⁻¹ cm⁻¹) at about 335 nm in *n*-hexane and 345 nm in acetonitrile can be assigned to the strongly allowed $\pi\pi^* \leftarrow S_0$ transition of the closed enol form (with the -OH group in the ring). The observed transition energy and intensity are in reasonable agreement with the computed values for the S_3 ($\pi\pi^*$) $\leftarrow S_0$ transition, Table 1. Consistent with the $\pi\pi^*$ -state proton transfer, yielding a keto tautomer (with the carbonyl group in the ring), the steady-state fluorescence in *n*-hexane, as well as in acetonitrile, are strongly Stokes shifted (~ 525 nm in *n*-hexane and 545 nm in acetonitrile) with respect to the 335/345 nm $^1\pi\pi^* \leftarrow S_0$ absorption of the enol form. The observed fluorescence of DMAHBA is very similar to the 510 nm proton transfer (PT) emission band of orthohydroxybenzaldehyde.⁹ The emission peak of 525/545 nm is in good accord with the computed vertical emission wavelength (523 nm) of the $\pi\pi^*$ state of the keto form, given in Table 3.

3.2.2. Picosecond Time-Resolved Fluorescence. Figures 5 and 6 present the picosecond time-resolved fluorescence spectra of DMAHBA in *n*-hexane and acetonitrile, which are obtained by the optical Kerr-gating setup (see section 2 for details).

Interestingly, for the time range as short as subpicoseconds, the molecule exhibits strong new fluorescence with intensity maximum at about 380 nm in *n*-hexane and at about 400 nm in acetonitrile. The ultrashort decays of the 380/400 nm emissions in Figures 5b and 6b indicate that the 380/400 nm emission can be assigned to the radiative transition of the $\pi\pi^*$ state of the enol form, Figure 3. The mirror-symmetry relationship of the emission with the strong $\pi^* \leftarrow \pi$ absorption at about 335/345 nm supports the assignment of the emitting state to the $\pi\pi^*$ state of H-L orbital transition (Table 3). The ultrafast decay time at the 380/400 nm fluorescence is consistent and the very rapid proton transfer of the $\pi\pi^*$ state of the enol to keto form (Figure 2a). Although the decay of the 380/400 nm emission is accompanied by the rise of 525/545 nm emission, the latter is slower than the former. This is consistent with the internal proton transfer to the keto form that involves a significant change in the geometry of the molecule.

Interestingly, the spectral shape of the 525/545 nm $\pi\pi^*$ -state fluorescence of the keto form remains unchanged with delay time, indicating that only one excited state is responsible for the 525/545 nm emission in *n*-hexane and acetonitrile. Consistent with the conclusion, the decay time of the fluorescence band is independent of the emission wavelengths in the region of 530–650 nm. The TCSPC measurements of the temporal behaviors of the fluorescence bands are shown in Figure 7. These results are at odds with the conclusion of Mahanta et al.¹⁵ that the fluorescence

Table 5. Summary of the Obtained Decay Constants (in picoseconds) of DMAHBA in *n*-Hexane (Hex) and Acetonitrile (Acn) Obtained from the Various Time-Resolved Spectroscopic Measurements

DMAHBA/Hex	TRFS ^a		TCSPC ^b		TAS ^c		
	380 nm	525 nm	400 nm	530 nm	360 nm	410 nm	500 nm
τ_1	<1	12.4(14) ^d (−13.5%) ^e	<10.6(1) ^f (+95.9%)		9.2(4) (+38.3%)	3.3(3) (+32.9%)	
τ_2		289.2(30) ^d (+86.5%) ^e	790.9(3) (+4.1%)	295.5(1)	319.2(76) (+61.7%)	319.1(70) (+67.1%)	~300(1)

DMAHBA/Acn	TRFS		TCSPC		TAS ^c		
	400 nm	550 nm	410 nm	530 nm	375 nm	465 nm	530 nm
τ_1	<1	17.2(18) (−21.0%) ^e	<8.3(1) ^f (+94.0%)		12.3(5) (+45.1%)		
τ_2		235.4(28) (+79.0%) ^e	391.2(2) (+4.7%)	200.7(3)	278.6(70) (+54.9%)	298(4)	~340(1)

^a Picosecond time-resolved fluorescence spectra using an optical Kerr-gating, followed by fluorescence wavelengths of interest. ^b Time-correlated single photon counting with monitoring wavelengths. ^c Femtosecond transient absorption spectra with specific transients. ^d Fit time constant for the fluorescence decay curve with a standard deviation (1σ) in the parentheses. ^e Multiexponential fits are indicated with component ratios of their pre-exponential scalar factors in the parentheses. A negative sign in the ratio indicates a rising contribution. A long-live component ($\sim$ nanoseconds) due to the triplet absorption was treated as the background constant A_∞ in the fitting function $\sum_i A_i \exp(-t/\tau_i) + A_\infty$, which was analytically convoluted with a Gaussian function. ^f The derived time-constant of the short-decaying component is uncertain due to the time resolution (~ 30 ps) of TCSPC measurements.

Figure 8. Time-resolved transient absorption spectra and their temporal profiles of DMAHBA in *n*-hexane at room temperature (a–c). Arrows in (a) indicate the time-evolution of the spectra (−10–150 ps, with an interval of 1 ps) and assignments for the transient are shown. (b) Temporal profiles of the assigned transients for DMAHBA, which were extracted with a band-integration from the spectra. Leaders show the decay time constants by the fits (see details in Table 5). (d) Time-resolved transient absorption spectra of DMABA in *n*-hexane at shorter time delay (0–25 ps) for comparison to DMAHBA. The triplet–triplet absorption bands, $T(\pi\pi^*)$, at 430/450 nm grows rapidly as the $n\pi^*$ transient at 345 nm decays, and then $T(\pi\pi^*)$ bands decay at about 11 ns in later times of TA spectra (not shown).

decay is biexponential in acetonitrile. The absence of the ICT fluorescence is consistent with the extremely small oscillator strength of the TICT state ($f \sim 10^{-3}$) in both enol and keto forms, which would

render the quantum yield of the TICT fluorescence negligibly small. Table 5 summarizes the detailed decay constants for the time-resolved fluorescences and time-resolved excited-state absorptions.

Figure 9. Time-resolved transient absorption spectra and their temporal decay profiles of DMAHBA (a–c) in acetonitrile at room temperature (a–c). Arrows indicate the time-evolution of the spectra (–10–200 ps with an interval of 1 ps), and assignments for the transient are shown. (b) Temporal profiles of the assigned transients for DMAHBA, which were extracted with a band-integration from the above spectra. The negative absorption at the red wavelength is due to the stimulated emission (SE) of the molecule. Leaders show the fit decay times (see details in Table 5). (c) TA spectra at longer pump–probe time-delays. The dashed curve is the ground-state absorption spectrum of benzaldehyde radical anion ($\text{BA}^{\bullet-}$), adopted from ref 21 with permission, whose ordinate is not scaled. (d) Time-resolved transient absorption spectra of DMABA in acetonitrile at longer delay times for comparison to DMAHBA.

3.2.3. Time-Resolved Excited-State Absorption. Figure 8a,c presents the picosecond transient absorption (TA) spectra of DMAHBA in *n*-hexane, following the $\pi\pi^* \leftarrow S_0$ excitation at 315 nm. The observed TA spectrum in *n*-hexane is composed of an intense feature at about 355 nm and a weaker broad feature at longer wavelengths. The strong 355 nm TA, which is very similar to the 345 nm picosecond $n\pi^*$ transient of the closely related 4-dimethylaminobenzaldehyde (DMABA), Figure 8d, can be assigned to the absorption spectrum of the S_1 ($n\pi^*$) state of enol form, which is predicted to lie at about 390 nm, Table 4. The triplet–triplet absorption of the T_1 ($\pi\pi^*$) state at about 450 nm is evident in DMABA. The weaker TA features in between 400 and 600 nm of DMAHBA can be assigned to the $\pi\pi^*$ state of the keto form, by comparison with the predictions of the TDDFT calculations, Table 4. Consistent with this assignment, the decay time (~ 300 ps) of the TA of DMAHBA in *n*-hexane at 500 nm, Figure 8b, is very similar to that (~ 296 ps) of the 530 nm fluorescence from the $\pi\pi^*$ state of the keto form, Figure 7b. For the pump–probe delay times of up to a few hundred picoseconds, the TA spectra of DMAHBA in *n*-hexane decays without significant change in spectral shape. At longer delay times, for example, ~ 1 ns, the presence of the shoulder at about 550 nm is not evident, as shown in Figure 8c, indicating that the weak broad feature of the TA spectra is not due to the $\pi\pi^*$ state of the keto form. We attribute the long-lived TA in the 550 nm to about 400 nm to the T_n ($\pi\pi^*$) $\leftarrow T_1$ ($\pi\pi^*$) absorption.

In acetonitrile, the time-resolved TA spectra have more structures, Figure 9a. As in *n*-hexane, there is the sharp TA due to the $n\pi^*$ state of the enol form, which appears at 375 nm in acetonitrile. The TA spectra at longer wavelengths have distinct features at about 475 nm and at about 530 nm at long delay times, which are very similar to the picosecond TA of DMABA that has been assigned to the TICT state.¹⁶ The comparison shown in Figure 9c,d indicates that the 475/530 nm transients of DMAHBA in acetonitrile are due to the TICT-state absorption of the molecule in the enol form. The decay rate of the TICT state is ~ 340 ps, which is significantly longer than the 200 ps decay time of fluorescence from the $\pi\pi^*$ state of keto form (Figure 7d). The results of the TA experiments in acetonitrile are therefore consistent with the occurrence of coupled proton and electron transfer in DMAHBA, which is predicted by the TDDFT calculations.

It is interesting that the formation of the triplet state is much less efficient in DMAHBA than in the closely related DMABA, Figures 8 and 9. This is consistent with the very rapid proton transfer in the initially excited $\pi\pi^*$ state of DMAHBA in enol form, which significantly reduces the efficiency of internal conversion to the S_1 ($n\pi^*$) state of DMAHBA in the enol form.

In both *n*-hexane (Figure 8a) and acetonitrile (Figure 9a), there is the presence of stimulated emission in the TA spectra, which is particularly evident on the red end (>550 nm). The presence of this negative contribution to the decay times of the TA discussed herein is however thought to be not serious.

4. CONCLUSIONS

We have investigated proton and electron transfer processes in 4-dimethylamino-2-hydroxy-benzaldehyde (DMAHBA), following photoexcitation of the S_0 molecule of the enol form into its $\pi\pi^*$ state.

The TDDFT calculations of the excited electronic states indicate that the $\pi\pi^*$ states of the enol form are unstable with respect to the proton transfer. The $\pi\pi^*$ state of the keto form, resulting from the proton transfer, is the primary emitting state of DMAHBA in both *n*-hexane and acetonitrile. The TD/B3LYP/cc-pVDZ vertical electronic energy of the $\pi\pi^*$ state of the keto form is calculated to be 2.37 eV (523 nm), which is in excellent agreement with the observed fluorescence at 2.36 eV (525 nm). The very short-lived fluorescence from the $\pi\pi^*$ state of the enol form has been observed at about 380 nm in *n*-hexane and at about 400 nm in acetonitrile, in very good agreement with the predicted peak wavelength of 380 nm. The observed transient absorption (TA) of the $n\pi^*$ state of enol form at about 355/375 nm is consistent with the TDDFT calculation, which predicts the $n\pi^*$ transients at 386 and 398 nm.

In *n*-hexane, photoexcited DMAHBA exhibits only proton transfer, with the $\pi\pi^*$ state of the keto form exhibiting TA in the range of 400–570 nm and fluorescence at about 525 nm. Both the TA and the fluorescence decay with the identical lifetime of ~ 300 ps. The TA of the $n\pi^*$ state of the enol form decays in about 10 ps.

In acetonitrile, DMAHBA exhibits coupled sequential proton and electron transfer. The TD/B3LYP/cc-pVDZ calculation predicts a small energy barrier of about 3 kcal/mol for transformation of the $\pi\pi^*$ state of keto form to the more stable twisted intramolecular charge transfer (TICT) state, in which the positively charged dimethylamino group lies perpendicular to the negatively charged benzaldehyde ring. The keto form of TICT state is however predicted to be less stable than the enol form of the TICT state. Consistent with this prediction, the TA spectra of DMAHBA in acetonitrile displays features that are very similar to the benzaldehyde radical-anion-like TICT state of 4-dimethylaminobenzaldehyde (DMABA). The TICT state of the enol form of DMAHBA decays to the ground state with a lifetime of ~ 340 ps, which is significantly longer than the decay time (~ 200 ps) of the fluorescence from the $\pi\pi^*$ state of the keto form. This solvent-polarity dependence of TICT-state formation is very similar to that which has been observed in DMABA.¹⁶

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