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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

## Observation of Excited State Proton Transfer Reactions in 2-Phenylphenol and 2-Phenyl-1-naphthol and Formation of Quinone Methide Species

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The excited state intramolecular proton transfer (ESIPT) reactions from a phenol (naphthol) to a carbon atom in the adjacent aromatic ring of 2-phenylphenol (**1**) and 2-phenyl-1-naphthol (**4**) are prototypical examples of intramolecular proton transfer not mediated by solvent molecules. Femtosecond time-resolved transient absorption (fs-TA) studies are conducted for the first time to directly probe the formation of quinone methide (QM) species generated from the ESIPT pathways of **1** and **4**. Steady-state absorption experiments demonstrated **1** exists mainly in its non-deprotonated form in neat MeCN and in water-MeCN solutions. Observation of the phenolate form in water-containing solution (MeCN-H<sub>2</sub>O, 1:1, v:v) in fluorescence spectra demonstrates the occurrence of an ESPT reaction between **1** and the surrounding water molecules. In neat MeCN a transient species that absorbs around 520 nm was detected in fs-TA spectra and was assigned to the QM species formed by ESIPT to the 2'-position. This transient signal is strengthened in cyclohexane. In a water-MeCN solution, an additional transient species assigned to the QM species at the 4'-position of **1** was also detected that absorbs around 485 nm. Similar results for **4** were observed, with the absorbance of the transient species being more intense, which suggests there is more efficient production of the QM species from **4**, consistent with quantum yields for deuterium exchange in the distal ring reported for these compounds.

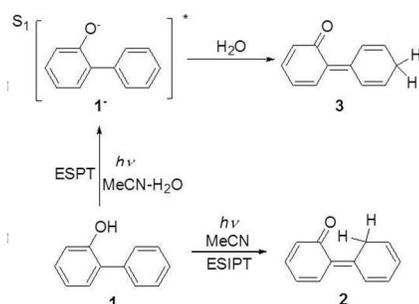
### Introduction

Proton transfer is an important and elementary process in numerous areas of biology and chemistry. In particular, excited state proton transfer (ESPT) is of fundamental interest and has been a hot topic for many research groups.<sup>1</sup> When an aromatic molecule contains both acidic and basic sites which upon excitation exhibit enhanced acidity and basicity, respectively, an excited state intramolecular proton transfer (ESIPT) can take place. Additionally, quinone methides (QMs) are important intermediates and have become a subject of significant scientific interest.<sup>2</sup> It has been demonstrated that QMs react with amino acids<sup>3</sup> and DNA,<sup>4</sup> and the ability of QMs to alkylate and crosslink DNA<sup>5,6,7</sup> make them potent agents in cancer therapy. QM can be generated in thermal reactions by oxidation of phenols,<sup>8</sup> extrusion of water and other small molecules from hydroxybenzyl alcohols,<sup>9</sup> and fluoride induced desilylation.<sup>10</sup> Using milder approaches,<sup>11</sup> QM can be formed in photochemical reactions of suitably substituted phenols, such as photodehydroxylation of hydroxybenzylphenols<sup>12</sup> photoelimination of acetic acid<sup>13</sup> or amines.<sup>14</sup> In some of these methods, ESPT and ESIPT are invoked in the mechanisms of QM formation. Thus, observation of QMs from ESPT and/or ESIPT reactions and elucidation of the mechanism(s) of their formation are important to obtain in order to better understand how QMs are formed and

what fundamental processes are involved in determining the yields and product outcomes.

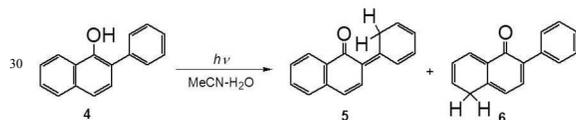
Among the reported ESIPT reactions, the usual acidic site is a phenolic proton, and the basic site is normally a heteroatom on a heterocyclic ring,<sup>15</sup> or a carbonyl group.<sup>16</sup> Unusually, the carbon atom has been discovered to serve as a basic group. The first example of an ESPT reaction between a phenol OH and a carbon atom was reported by Yates and co-workers when studying the photohydration of styrenes and arylacetylenes.<sup>17</sup> About a decade ago, Wan and co-workers reported the ESIPT reaction of 2-phenylphenol (**1**) from the phenol moiety to the carbon of the benzene ring not bearing the hydroxyl group (see Scheme 1) through a pathway that is not mediated by solvent molecules.<sup>18</sup> The occurrence of ESIPT reactions for **1** generating QM species was inferred due to the regiospecific incorporation of deuterium upon irradiation in D<sub>2</sub>O (D-exchange  $\Phi = 0.041$ ).<sup>18</sup> D-exchange of **1** at the 2'-position proceeds via QM **2**, whereas exchange at the 4'-position takes place via QM **3**. It was deduced that formation of QM **3** requires water to mediate the formal proton transfer (an initial ESPT to solvent water, followed by a re-protonation at the 4'-position), while water was not essential for ESIPT giving QM **2**. Besides the known enhanced acidity of phenols in the excited singlet state, singlet state reactivity is further supported from the correlation of the fluorescence

intensity and the lack of noticeable oxygen quenching with the observed D-exchange.<sup>18</sup> Considerable research efforts have been devoted to transiently record the electronic spectra of the proposed QMs **2** and **3** generated in ESIPT and ESPT reactions using nanosecond laser flash photolysis,<sup>18</sup> but unfortunately have so far proved unsuccessful.



Scheme 1. ESPT and ESIPT reactions of **1**.

A more recent study of ESIPT of 2-phenyl-1-naphthol (**4**) showed a remarkably high quantum yield for deuterium exchange of 0.7 (see Scheme 2).<sup>19</sup> The transient absorption spectrum of QM intermediates on the nanosecond time scale were observed and reported as the first optical detection of a QM species formed by ESIPT to an aromatic carbon atom.<sup>19</sup> However, there is no reported transient absorption study on the ultrafast time scale for such reactions.



Scheme 2. ESIPT and ESPT reactions of **4**.

A particular strength of the femtosecond transient absorption (fs-TA) technique is its ability to directly detect and characterize the transient intermediates with short lifetimes. Herein, we present fs-TA studies on **1** and **4**. **1** was selected as a model compound to start our ultrafast spectroscopic study due to several considerations. An obvious aspect is that **1** is commercially available. It was also the first compound that was discovered to undergo ESIPT from a phenol group to a carbon atom on an aromatic ring. Furthermore, several derivatives of **1** have been exploited as probes to study the specific characteristics of protein binding sites.<sup>20</sup> Fs-TA studies were also performed for **4** which is the derivative that undergoes the most efficient ESIPT from the phenolic OH to a carbon atom. This real-time detection of QM species by ultrafast TA spectroscopy provides evidence of the ESIPT process of **1** and **4**, leading to an improved understanding of the reaction mechanisms for this method for photochemical generation of QMs.

## Experimental and Computational Methods

2-Phenylphenol was purchased from Sigma and used without further purification. 2-Phenyl-1-naphthol was prepared from methyl 2-phenylacrylate and phthalide according to the known procedure. Sample solutions for the experiments described in this work were prepared using spectroscopic grade acetonitrile

(MeCN) and deionized water. NaOH was used to make an alkaline sample solution with pH 12.

A. Steady-State Absorption and Fluorescence Experiments. Steady-state absorption spectra were recorded on a PerkinElmer Lambda 19 UV-vis spectrometer using a 1-cm path length quartz cuvette. Fluorescence emission spectra were obtained on a FL 600 spectrometer using the excitation wavelength of 266 nm.

B. Femtosecond Transient Absorption (fs-TA) Experiments. Fs-TA measurements were performed using a femtosecond regenerative amplified Ti:sapphire laser system. The amplifier was seeded with the 120 fs output from the oscillator. The probe pulse was generated by using about 5% of the amplified 800 nm output to generate a white-light continuum (350-800 nm) in a CaF<sub>2</sub> crystal. The probe beam was split into two before passing through the sample. One beam travels through the sample, the other was sent to the reference spectrometer monitored the fluctuations in the probe beam intensity. Fiber optics were coupled to a multichannel spectrometer. For the present experiments, the 40 ml solution in a flowing 2 mm path-length cuvette was excited by a 267 nm pump beam. The sample solutions for the fs-TA experiments were prepared to obtain an absorbance of 1 at 267 nm, in that way, the same number of photons was absorbed for the same irradiating conditions in each case.

C. Nanosecond Time-Resolved Transient Absorption (ns-TA) Experiments. The ns-TA measurements were carried out on a commercial laser flash photolysis setup. The 267 nm pump laser pulse was obtained from the fourth harmonic output of an Nd:YAG laser, and the probe light was provided by a 450 W Xenon lamp. The sample was excited by the pump laser and at a right angle the probe light from the Xenon lamp was passed through the sample. The two beams were focused onto a 1 cm quartz cell. The transmitted probe light was then measured either by a single detector (for kinetic analysis) or by an array detector (for spectral analysis). The changes in the transmission properties were normally converted into changes of optical density ( $\Delta OD$ ). The signals analyzed by a monochromator were detected by a photomultiplier and the signal processed via an interfaced PC and analytical software. Unless indicated the ns-TA experiments were done in air saturated solutions and the sample solutions were prepared with an absorbance of 1 at 267 nm.

D. Nanosecond Time-Resolved Resonance Raman (ns-TR<sup>3</sup>) Experiments. Ns-TR<sup>3</sup> experiments were performed using the apparatus and methods described previously and a short description is given. A 266 nm pump wavelength (by the fourth harmonic of a Nd:YAG nanosecond pulsed laser) and the 368.9 nm probe wavelength (by the second anti-Stokes hydrogen Raman-shifted laser line produced from the second harmonic of a second Nd:YAG laser) were used. The pump pulse excited the sample to initiate the photochemical reactions and the probe pulse interrogated the sample and the intermediate species produced. The laser beams were lightly focused and aligned so that they were overlapped onto a flowing liquid stream of sample. A pulse delay generator was employed to electronically control the time delay between the pump and probe laser. Raman scattered light was acquired using a backscattering geometry and detected by a liquid nitrogen-cooled charge-coupled device (CCD) detector. The TR<sup>3</sup> signal was acquired for 10 s by the CCD before being

read out to an interfaced PC computer and 10 scans of the signal were accumulated to produce a resonance Raman spectrum. The ns-TR<sup>3</sup> spectra presented were obtained from subtraction of an appropriately scaled probe-before-pump spectrum from the corresponding pump-probe resonance Raman spectrum to remove non-transient bands. The Raman bands of MeCN were employed to calibrate the Raman shifts with an estimated accuracy of 5 cm<sup>-1</sup>. The sample concentrations in ns-TR<sup>3</sup> were ~5 × 10<sup>-4</sup> M.

E. Density Functional Theory (DFT) Calculations. The optimized geometry, vibrational modes, and vibrational frequencies for the interested species were obtained from (U) B3LYP/ 6-311G\*\* DFT calculations. No imaginary frequency modes were observed at any of the optimized structures shown here. A Lorentzian function with a 15-cm<sup>-1</sup> bandwidth was used with the computed Raman vibrational frequencies and their computed relative intensities to determine the (U) B3LYP/ 6-311G\*\* calculated Raman spectra to compare with the corresponding experimental resonance Raman spectra. TD-DFT methodology is used to compute the low-lying excited states of transient species interested. GaussSum software was utilized to simulate the UV-Vis spectra. The polarizable continuum model (PCM) was used for evaluating the (bulk) solvent effects. All of the calculations were executed using the Gaussian 03 program suite installed on the High Performance Computing cluster at the Computer Centre in The University of Hong Kong.

## Results and Discussion

### A. Ultrafast Spectroscopic Study for 1

The steady-state absorption and fluorescence spectra were acquired for **1** in MeCN and aqueous solutions (Figure 1S). Under both conditions, **1** exists solely as its non-deprotonated form and absorbs at 286 nm. The emission band from the non-deprotonated form of **1** is observed at 330 nm in MeCN. An extra emission band at 415 nm, as expected for the singlet phenolate species, is detected in aqueous solution. Observation of the phenolate in water-containing solutions suggests the occurrence of the ESPT reaction between **1** and the solvent water molecules. This can be reasoned by the enhanced acidity of the phenol group in the excited state (pK<sub>a</sub> for **1** = 1.15 ± 0.04).<sup>21</sup>

#### Ultrafast Spectroscopic Study of **1** in MeCN.

Having an electron donor group OH, **1** has considerable fluorescence emission which makes it very difficult to do a time-resolved resonance Raman (TR<sup>3</sup>) study to gain vibrational structure information. Therefore, fs-TA and nanosecond-TR<sup>3</sup> experiments were conducted for a reference compound 2-fluorobiphenyl (**7**) to help gain some insight into the photophysical and photochemical pathways of **1**.

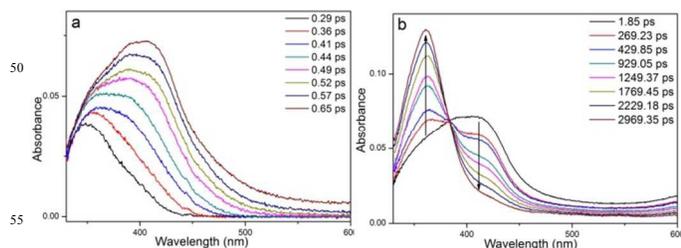


Figure 1. The fs-TA spectra of **7** in MeCN acquired after 267 nm irradiation.

Figure 1 displays the fs-TA spectra of **7** obtained in MeCN. Upon irradiation, **7** is excited to its S<sub>n</sub> state. The transformation time and the spectral profile changes indicate the process taking place for the first 1 ps can be attributed to the internal conversion (IC) from S<sub>n</sub> to the lowest singlet excited state (S<sub>1</sub>). Then, observation of a well-defined isosbestic point at 383 nm indicates a dynamic transformation from the S<sub>1</sub> species to another one with an absorption band situated at 360 nm. Because the triplet biphenyl was reported to have intense absorption around 370 nm,<sup>22</sup> it is therefore likely that the new species detected at 360 nm is probably the triplet **7** originating via an intersystem crossing (ISC) process. To gain corroboration for this assignment, an ns-TR<sup>3</sup> experiment was conducted for **7** in MeCN (see Figure 2S, supporting information). Examination of Figure 2S reveals that mainly one species was observed, and it is revealed to be the triplet **7** by comparison with the simulated Raman spectrum (see Figure 3S). Thus, it is straightforward to assign the transformation in the fs-TA spectra as the ISC process and the transient species with absorption band at 360 nm as the triplet **7** intermediate. Observation of the ISC process and the triplet state of **7** is consistent with the studies on biphenyl and its derivatives.<sup>23,24,25,26</sup>

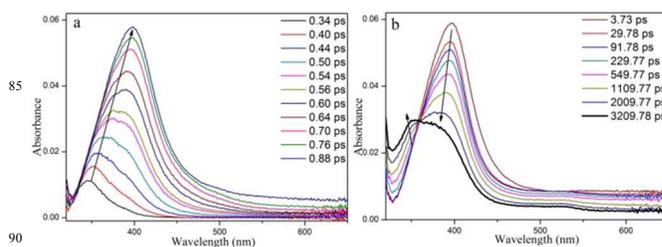


Figure 2. Shown are the fs-TA spectra obtained for **1** in MeCN acquired after 267 nm irradiation.

Figure 2 displayed the fs-TA spectra of **1** recorded in MeCN. The first transient species with absorption band at 346 nm (onset at ~320 nm) is assigned to be the S<sub>n</sub> state of **1**, and is quickly converted to S<sub>1</sub> with an absorption band that is gradually bathochromic shifted up to 398 nm within 1 ps via an IC process. Then, the S<sub>1</sub> species of **1** decayed with a new species produced with a broad band around 350 nm, which is also detected in the ns-TA spectra (see Figure 4S) recorded under the same reaction conditions. Combining these results with results from the time-resolved studies on **7**, the absorbance around 350 nm should have most of its contribution from the triplet excited state of **1**. The resemblance of the triplet spectra of **1** with that of the triplet **7** indicates the triplet excitation is localized on the biphenyl group. The bleaching band at 330 nm correlates with the steady-state fluorescence results. Nanosecond emission experiments were conducted in MeCN and an emissive species was observed at 330 nm. This is consistent with the static fluorescence results showing that the non-deprotonated form of **1** is the only species contributing to the emission band. As the delay time increased, two differences were detected for **1** (compared to **7** recorded under analogous experimental conditions). A bump at 525-nm

was observed, whereas the 398 nm absorbance did not decay to zero as the triplet state of **1** grows in. We think the absorption band at 525 nm arises from the intermediate QM **2** (see Scheme 1) in light of the results of Wan and co-workers previous studies, which evidenced the occurrence of the ESIPT process in **1** under analogous experimental conditions.<sup>18</sup> To gain further support, fs-TA experiments for **1** were performed in cyclohexane (Figure 5S) where a two-fold enhancement in the *ortho* exchange was observed from the deuterium exchange experiment.<sup>18</sup> Examination of Figure 5S suggests that at post delay times, a transient species with an absorbance at 400 and 525 nm was formed via the singlet excited state of **1** and its absorbance was more pronounced in intensity than that in MeCN. This result is in accord with the work conducted by Wan and coworkers.<sup>18</sup> Time-dependent density functional theory calculations (TD-DFT) can do a reasonably good job of reproducing the general features of the absorption spectrum of QM **2** (Figure 6S). Based on these results, the transient species absorbing at 400 and 525 nm in MeCN can be reasonably assigned to QM **2**. The fs-TA study directly probes the occurrence of the ESIPT reaction for **1** in MeCN and demonstrates the generation of the QM **2** species via the singlet excited state.

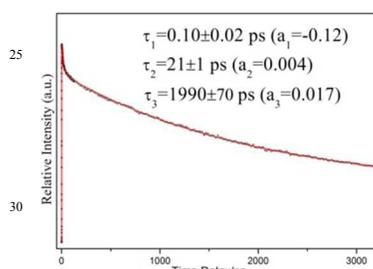


Figure 3. Shown is the time-dependence of the transient absorption for **1** in MeCN at 400 nm. The red solid lines indicate the kinetics fitting to the experimental data (circles) with a tri-exponential function.

For the weak absorbance of QM **2** at 525 nm, the kinetic analysis was done for the 400 nm wavelength to fit the experimental data in order to better understand the parallel photophysical reactions of **1** (see Figure 3). The time constant of  $\tau_1=100$  fs is assigned to the IC process from  $S_n$  to  $S_1$  and it is consistent with a typical IC time scale.<sup>27</sup> For the decay component, as analyzed, the excited singlet state of **1** in MeCN and cyclohexane mainly deactivates via three channels: an ISC process, to give the excited triplet state species with absorption around 350 nm, the radiative decay process to the ground state species with an emission at 330 nm, and the ESIPT reaction, to give QM **2** with an absorption around 400 and 525 nm. However, a three term function was not needed to fit the decay experimental data at 400 nm (see Figure 7S). This can be accounted for by the fact that there is some contribution from the generated QM **2** species to the absorbance around 400 nm and this may offset the decay contribution at the same position. Expectedly, a bi-functional term can do an adequate job for the decay fitting. The constant  $\tau_2=21$  ps is attributed to the ISC process. The constant  $\tau_3=1990$  ps is tentatively assigned to the  $S_1$  to  $S_0$  process which is in good agreement with a literature value

(1.8 ns).<sup>21</sup> The absorption at 385 nm was also analyzed and a similar result was obtained (Figure 8S). Although an accurate rate constant for the ESIPT of **1** was not successfully obtained, the lifetime of QM **2** is estimated to be very short (from several hundreds of picoseconds to several nanoseconds) because QM **2** was only detected in the fs-TA spectra and mainly the triplet **1** was observed only within the resolution of the ns-TA experiments.

#### Ultrafast Spectroscopic Study of **1** in an Aqueous Solution.

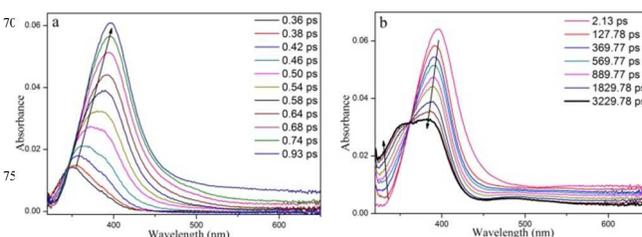


Figure 4. Shown are the fs-TA spectra obtained for **1** in MeCN- $H_2O$  (1:1, v:v) solution acquired after 267 nm irradiation.

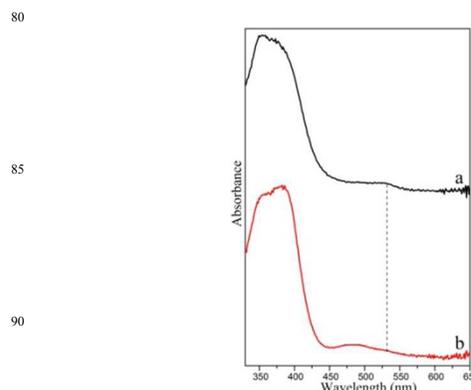


Figure 5. Comparison of the fs-TA spectra of **1** in (a) MeCN at the delay time of 3210 ps, (b) MeCN- $H_2O$  (1:1, v:v) at the delay time of 3230 ps.

Figure 4 displays the fs-TA spectra of **1** obtained in water-containing solution. In analogy with the results for **1** in MeCN, the formation of the  $S_1$  species was observed to occur via the IC process and subsequently  $S_1$  decayed to produce its triplet excited state that has an intense absorption band around 350 nm. Examination of the spectrum recorded at late delay times (Figure 5b) reveals that in addition to the typical absorption band for QM **2** at 525 nm related with the ESIPT process a new species was also observed around 480 nm. As is evident from the static fluorescence study showing the ESPT reaction of **1** in water-containing solutions, the species situated at 480 nm is proposed to be the species QM **3** related with the ESPT reaction as shown in earlier studies by Wan and coworkers.<sup>18</sup> TD-DFT calculations were performed (Figure 9S) and these results exhibited reasonable correlation with the experimental results. The assignment of the 525 nm absorption to QM **2** and the 480 nm absorption to QM **3** are consistent with the structurally similar QM species observed in a previous report,<sup>28</sup> since QM **2** with a more linearly conjugated system should absorb at a longer wavelength compared to QM **3**. It is noted that the absorbance of

the triplet **1** in an aqueous solution is less intense than in MeCN, suggesting the ISC process for **1** faces more competition from other decay pathways in a water-containing solution, which could be attributed to competition from the ESPT reaction.

### B. Ultrafast Spectroscopic Study for **4**

With the experience gained in the analysis for **1**, an ultrafast transient absorption study was conducted for **4**.

#### Ultrafast Spectroscopic Study of **4** in MeCN.

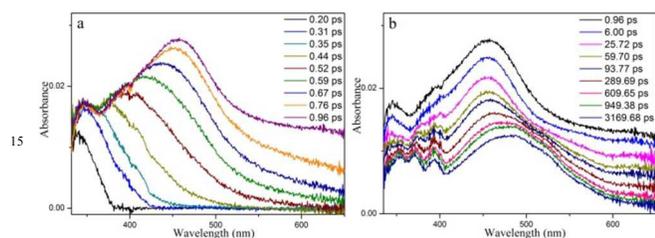


Figure 6. The fs-TA spectra of **4** in MeCN acquired after 267 nm irradiation.

Figure 6 shows the fs-TA spectra of **4** recorded in MeCN. The pump wavelength 267 nm used in fs-TA experiments excited **4** to its  $S_n$  state and the first transient species that has an absorption band at 348 nm is attributed to the  $S_n$  state of **4**.  $S_n$  is quickly converted to  $S_1$  that has an absorption band around 458 nm. Afterwards,  $S_1$  of **4** decayed to produce a new species that has a broad band centered around 485 nm which exhibited an identical spectral profile with the species QM **5** ( $\tau \sim 20$  ns) detected in the ns-TA experiments by Wan and coworkers under analogous conditions.<sup>19</sup> Consequently, we assign the observed transient species to QM **5** with further support from the results of TD-DFT calculations (see Figure 10S). These results support an assignment of the signal at 525 nm as direct spectroscopic evidence of QM from ESPT in MeCN.

#### Ultrafast Spectroscopic Study of **4** in Aqueous Solution.

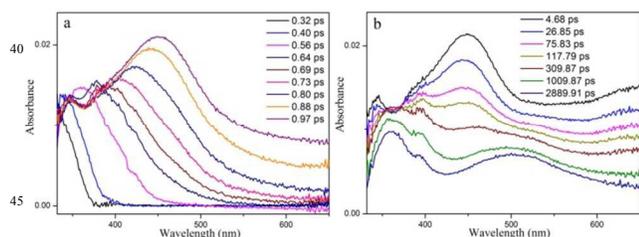


Figure 7. The fs-TA spectra of **4** in MeCN-H<sub>2</sub>O (1:1, v:v) solution acquired after 267 nm irradiation.

Figure 7 shows the fs-TA spectra of **4** recorded in water-containing solution. As the singlet excited state of **4** was formed, it transferred to new species that has an absorbance centered at 510 nm.

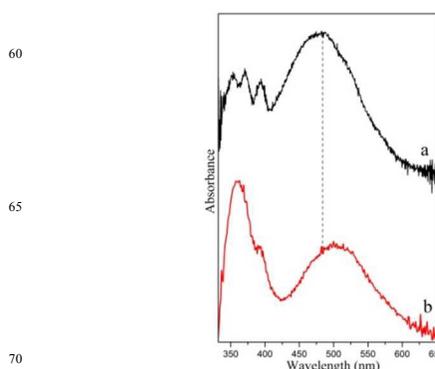


Figure 8. Shown is a comparison of the fs-TA spectra of **4** in (a) MeCN at a delay time of 3210 ps, (b) MeCN-H<sub>2</sub>O (1:1, v:v) at delay time of 3230 ps.

The transient absorption spectrum obtained at a late delay time for **4** in water-containing solutions was compared to that recorded in MeCN (Figure 8). Similar to the studies on **1**, the emission from the naphtholate species of **4** was observed under this experimental condition, suggesting the occurrence of the ESPT reaction between the substrate and solvent water molecules. We therefore propose that some amount of the QM species at the distal carbon site with the corresponding QMs **6** was produced coexisting with QM **5** generated from the ESPT process. To make things clear, the spectrum recorded at late time delays was compared with that recorded in MeCN (Figure 8). Expectedly, the transient absorption information of QM **5** was recognizable besides another species that had a red-shifted absorption band. TD-DFT calculation result for QM **6** is given in Figure 11S and appears consistent with these results.

Both reported D-exchange experiments and the above time-resolved spectroscopic results suggest that the ESPT reaction is remarkably efficient for **4** compared to **1**. It is therefore worth discussing the controlling factors leading to the different behaviors of these two compounds. First, it is noted that the ESPT reaction requires a reactive twisted conformation of the biaryl compound in the ground state, which allows for the overlap between the  $s$ -orbital of the phenol OH and the adjacent aromatic  $\pi$ -system.<sup>29</sup> We also studied the optimized geometries for the ground states of **1** and **4** (see Figure 12S). It is indicated by the results of these DFT calculations that the twist angle in **1** (54.38) is comparable to that in **4** (54.21), suggesting that the geometry effect does not vary much for the two compounds. Second, Basarić and Wan investigated the ESPT and solvent-assisted ESPT in isomeric phenyl naphthols and naphthyl phenols by preparative photolysis in MeCN-D<sub>2</sub>O, fluorescence spectroscopy, laser flash photolysis, and ab initio calculations. Those results show that the efficiency of the ESPT and solvent-assisted PT is mainly determined by different populations of the reactive conformers in the ground state and the NEER principle.<sup>30</sup> Third, the unproductive ISC process is revealed to be a competing pathway for the ESPT reactions. The efficiency of the ISC process can be a key determinant of the QM generation efficiency for **1** and **4**. It is manifested that the ISC transformation from the singlet excited state to the triplet excited state is efficient for **1**, while the ISC process with the generation of the triplet excited state of **4** is not obviously detected and seldom reported. Fourth,

the competition from the ESPT reaction in water-containing solutions is another competing pathway to the ESIPT reaction of interest.

In this work and previous publications from Wan's group, the term ESIPT is used to denote the true intramolecular proton transfer that is not mediated by solvent molecules, whereas ESPT is used to describe the process mediated by solvent. In these ESPT examples, a proton is transferred to a protic solvent giving phenolate (charged species) which undergoes protonation and subsequently forms QM. Although there is an additional charged intermediate, the overall reaction takes place between two neutral molecules. There are possible doubts with respect to the terms ESIPT and ESPT and the question whether it is really a transfer of a proton or an H-atom. The answer to this question can be obtained from calculations. The pre-requisite for the proton transfer is the formation of the charge transfer state. In our opinion, the term ESIPT to denote the intramolecular proton transfer between two neutral forms (as in the formation of **2** and **5**) without additional intermediates or solvent molecules is correct, taking into account that it takes place in a very polarized excited state. According to some related calculations (see reference 19), there is a significant charge transfer character in the S<sub>1</sub> state of **4** which is the driving force for the proton transfer.

## Conclusions

We would like to re-emphasize that the main objective of the current investigation is to gain ultrafast spectroscopic evidence for the QM intermediates generated in the ESPT and ESIPT reactions of **1** and **4** by fs-TA spectra. Although the quantum yield of the ESIPT and ESPT reactions of **1** are low, this compound is important to be studied as a convenient and inexpensive easy way to open the investigation of the QM species generated from the phenylphenol substrate. By measuring the fs-TA in respective aprotic solvent MeCN and water-containing solutions, we have been able to track the pathways of the excited state of **1** and **4**. The results unambiguously point to the formation of QM species. As far as we are aware, this is the first fs-spectroscopic evidence of QM species generated from **1** and **4**. The singlet excited state is unraveled to be the reactive state to undergo the ESIPT and ESPT reactions, which is in a good agreement with previous oxygen quenching experiments conducted by Wan and coworkers.<sup>18</sup> Ultrafast spectroscopic studies on **4** with efficient generation of QM species allows us to probe the ESIPT reaction on one hand and provide further evidence for the assignment of the **1** on the other hand.

## Notes and references

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† Electronic Supplementary Information (ESI) available: UV-Vis absorption and fluorescence spectra of **1**, ns-TR<sup>3</sup> spectra of **7** in MeCN, comparison of the experimental Raman spectrum of **7** to the calculated normal Raman spectrum of the triplet excited state of **7**, ns-TA spectra of **1** in MeCN, fs-TA spectra of **1** in cyclohexane, simulated absorption spectra of QM **2** obtained from the TD-DFT calculation employing BPW91/6-311G(d,p), time-dependence of transient absorption spectra for **1** in MeCN at 400 nm, decay time-dependence of the transient absorption for **1** in MeCN at 385 nm, simulated absorption spectra of the triplet state of **3** from the TD-DFT calculation using B3LYP/6-311G\*\*, simulated absorption spectra of the QM **5** obtained from the TD-DFT calculation using B3LYP/6-311G\*\*, simulated absorption spectra of the QM **6** obtained from the TD-DFT calculation employing B3LYP/6-311G\*\*, schematic depiction of the optimized structures of the ground state of (a) **1** and (b) **4** obtained from B3LYP/6-311G\*\* DFT calculations. See DOI: 10.1039/b000000x/

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