

Nonlinear Solvent Water Effects in the Excited-State (Formal) Intramolecular Proton Transfer (ESIPT) in *m*-Hydroxy-1,1-diaryl Alkenes: Efficient Formation of *m*-Quinone Methides¹

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Abstract: The photohydration of hydroxy-substituted 1,1-diaryl alkenes **1–3** has been studied in aqueous CH₃CN solution. Evidence for formation of quinone methide intermediates was provided by product studies and by observation of its absorption spectrum by laser flash photolysis. For the meta isomers, the proposed mechanism of *m*-quinone methide formation probably involves a solvent-mediated (“proton-relay”) excited-state (formal) intramolecular proton transfer (ESIPT) from the phenol hydroxyl group to the β-carbon of the alkene moiety in neutral aqueous CH₃CN solution, either in a concerted manner or via two very fast steps. The *m*-quinone methides are then trapped by water to form the corresponding diaryl ethanol product with high overall quantum yield. Evidence for the ESIPT pathway was provided by fluorescence and LFP measurements. The addition of small amounts of water (<0.8 M in CH₃CN) decreased the fluorescence emissions of **1** and **2** with a concomitant increase in production of *m*-quinone methides. Stern–Volmer analyses of fluorescence data revealed a dynamic and a minor static quenching component, both of which involved a water trimer cluster. The degree of charge transfer from the phenol (phenolate) oxygen to the alkene β-carbon, which may be thought of as the driving force for this efficient ESIPT, is pronounced for the meta isomer in the excited state, consistent with Zimmerman’s “meta–ortho effect”. Alkenes **1** and **2** were shown to be more efficient in *m*-quinone methide photogeneration than the hydroxy-substituted benzyl alcohol **8**, which required conditions of higher water content for similar quantum yields.

Introduction

Excited-state proton transfers (ESPTs) have been extensively studied due to their fundamental interest as well as their potential applications.² They can act as probes of microscopic solvation and have revealed the presence of hydrogen-bonded solvent clusters.³ Fluorescence studies of intermolecular ionizations^{3,4} and proton-relay proton transfers⁵ have implied that solvent clusters can accept or donate protons and that they can mediate

excited-state intramolecular proton transfers (ESIPTs). Direct evidence for cluster involvement in ESIPT has been obtained in the gas phase, although these clusters may differ from those found in the liquid phase.⁶ Theoretical calculations have also been used to predict cluster stability and structure.⁷ Cyclic systems which allow the hydrogen bonds to approach linearity for optimum interaction are favored. The size of the cluster has been shown to depend on the distance between the proton acceptor and donor as well as on the threshold proton affinity, which depends on the solvent and the acidity and basicity of the substrate groups.^{4–7}

ESIPT occurs most readily for those molecules whose acidity and basicity of both the proton donor and acceptor groups, respectively, are enhanced upon excitation. ESIPT can readily lead to the formation of tautomers that are difficult to form via thermal methods.^{2,5,8,9} Kalandropoulos and Yates⁹ reported the efficient photohydration of *o*-hydroxystyrene, which was cited as the first clear example of an irreversible ESIPT. Due to the increased acidity of the phenol moiety and the simultaneous increase in basicity of the alkene moiety upon excitation, direct

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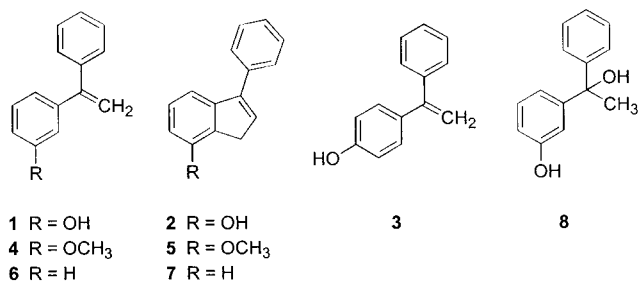
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ESIPT from the phenol moiety to the β -carbon of the alkene moiety occurred. The resulting *o*-quinone methide (*o*-QM) was trapped by water to form the aryl ethanol product. We decided to test the generality of using hydroxy-substituted styrenes as general QM precursors. Hydroxy-substituted 1,1-diaryl alkenes **1–3** were studied whose acid and base moieties are distal from each other. We show that photohydration of these substrates occurs efficiently in aqueous solution, and a solvent-mediated ESIPT is proposed as being involved in forming the corresponding QM intermediate. Previously, we have shown that hydroxy-substituted benzyl alcohols and related compounds can act as general QM photogenerators in aqueous solution.¹⁰ The mechanism involves an initial adiabatic dissociation to the phenolate, whose formation facilitates hydroxide loss at the benzylic position in a subsequent step. The relative photo-solvolytic quantum yields were in the order $o > m \gg p$. The methoxy derivatives, which can only form carbocation intermediates, showed much less or no reaction. In the present study, we show that **1–3** react significantly more efficiently than the corresponding hydroxy-substituted benzyl alcohols since the water-mediated ESIPT mechanism occurs even at low water concentrations, consistent with a concerted (or very fast) deprotonation–protonation process.



Results and Discussion

During the course of our studies of the photosolvolytic behavior of a variety of hydroxy-substituted benzyl alcohols, we found that several of these alcohols readily eliminated to the aryl alkene during their preparation. This led us to study the possible photohydration of **1–3**, to investigate the effect of a distal hydroxy substituent on the reaction and whether the corresponding QMs can be formed as intermediates. The α -phenyl group ensured a long enough lifetime of the generated QM (if formed) for detection by nanosecond laser flash photolysis (LFP). Compounds **4–7** were required for comparison purposes in fluorescence, LFP, and product studies since they lack the hydroxy substituent and thus have only the potential of leading to the carbocation (or possibly radical cation). Benzyl alcohol **8** was included to allow for a comparison between using hydroxy-substituted 1,1-diaryl alkenes vs hydroxy-substituted benzyl alcohols as potential QM precursors.

Product Studies. Photolyses were carried out using $\sim 10^{-3}$ M solutions of the substrates dissolved in 1:1 (v/v) aqueous H₂O–CH₃CN (Rayonet RPR-100 photochemical reactor; 254

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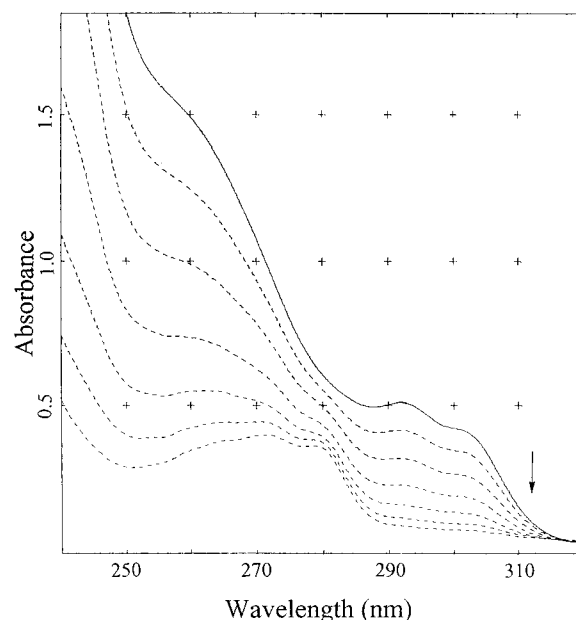
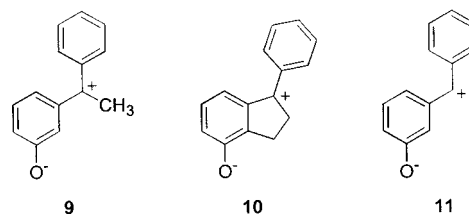
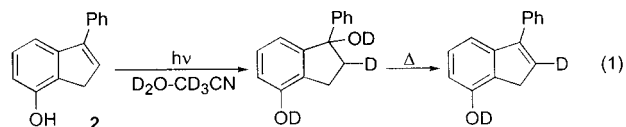


Figure 1. UV–vis traces for photohydration of **2** in 1:1 H₂O–CH₃CN. Each trace, after the first initial absorption, represents 5 min of photolysis at 254 nm.

nm lamps; ~ 15 °C; argon-purged solutions; 2–10 min irradiation). Photolysis of **1–3** yielded the corresponding diaryl ethanol (e.g., **8** from **1**) as the exclusive photoproduct, which is consistent with a *m*-QM (i.e., **9** from **1**) or a corresponding diarylmethyl carbocation intermediate being trapped by water.¹⁰ Initially, **2** appeared to be photostable in aqueous solution. However, irradiation in D₂O–CD₃CN revealed deuterium incorporation at the 2-position, even at low water concentrations (eq 1). Photolysis in an NMR tube, which allowed direct analysis



without workup, resulted in only diaryl ethanol formation. This indicated that the suspected *m*-QM intermediate **10** (or the corresponding diarylmethyl carbocation) did not re-form **2** but rather led entirely to the diaryl ethanol product, which dehydrated back to **2** on workup. Photohydration of **1** in H₂O–CH₃CN yielded the expected diaryl ethanol **8** cleanly, even at high conversions (>90%), without dehydration on workup. Also, photolysis in D₂O–CD₃CN showed only diaryl ethanol production and no deuterium incorporation at the β -position. This lack of a reverse proton transfer (from the β -carbon) is consistent with deprotonation of a carbon–hydrogen bond being generally slow in the ground state and, therefore, unlikely to compete with nucleophilic attack at the benzylic carbon.



The UV–vis absorbance of either **1** or **2** decreased smoothly on photolysis in H₂O–CH₃CN (Figure 1), the extent of which increased with increasing H₂O concentration (observable in the

0–1 M H₂O range). Hence, this provides a simple method for monitoring the extent of photohydration of these compounds. This absorbance loss was observed to be largest for H₂O, less for D₂O, and significantly less for CH₃OH (at the same concentration). This trend is consistent with direct involvement of H₂O (or CH₃OH) in the primary photochemical step. A similar study at high pH (pH > 10) revealed a decrease in absorbance loss (and hence photohydration yield) of either **1** or **2**, which is contrary to that observed for hydroxy-substituted benzyl alcohols, whose photosolvolysis quantum yields have been shown to increase at high pH due to direct excitation of the phenolate.¹⁰ This difference suggests that, for **1** and **2**, phenolate formation inhibits diaryl ethanol production, which is inconsistent with a stepwise mechanism in which the phenol dissociates adiabatically on excitation, followed by protonation of the alkene moiety.

Both **1** and **2** gave similar absolute quantum yields for formation of the corresponding diaryl ethanol ($\Phi_p = 0.22 \pm 0.02$ and 0.24 ± 0.02 , respectively in 1:1 H₂O–CH₃CN). These values are comparable to that reported for *o*-hydroxystyrene in 100% water ($\Phi_p = 0.19$).⁹ In contrast, **4** and **5** exhibited much lower quantum yields ($\Phi_p < 0.05$) for photohydration. Since the hydroxy and methoxy substituents have similar electronic effects, this difference in quantum yields implies that a different mechanism operates for each. Lacking any sort of electron-donating substituent, **6** did not photoprotonate under similar conditions, although the quantum yield for photohydration of the parent styrene has been reported to be 0.025 in 100% water at pH 7.^{11a} Only after extensive irradiation did **7** convert to an observable amount of the corresponding diaryl ethanol product. Relative quantum yields for conversion of **1** and **3** to their respective diaryl ethanol product were ~2.5 times less for the latter. Thus, **1** apparently generates the corresponding QM more efficiently, which is consistent with Zimmerman's "meta-ortho effect";¹² i.e., the greater electronic transmission effect of the *m*-hydroxy group in the excited-state allows more facile photoprotonation. The above results from product studies suggest that an ESIPT mechanism leading to *m*-QM for **1** and **2** is operative, rather than the less efficient direct photoprotonation¹¹ of the alkene moiety, leading to the carbocation observed for the methoxy-substituted and unsubstituted derivatives.

Laser Flash Photolysis (LFP). LFP of **1** or **8** in neat H₂O (pH 7) yielded the *same* strongly absorbing transient ($\lambda_{\max} = 425$ nm) whose decay ended at baseline and was fitted to a single exponential ($\tau = 47 \pm 1$ ns) (Figure 2). The lifetime and wavelength maximum of this transient are very similar to those observed for *m*-QM **11**, which we have previously characterized by LFP from the corresponding hydroxy-substituted benzyl alcohol.¹⁰ Although this transient absorbs in the same region as other arylmethyl carbocations, its lifetime is too long. Based on the results of the product studies and previous LFP data,¹⁰ the transient is assigned as **9**, whose deprotonated *m*-hydroxy group is strongly electron donating ($\sigma = -0.47$), in contrast to the protonated *m*-hydroxy group, which is electron withdrawing ($\sigma = +0.12$) and would thus lead to a shorter lifetime than the unsubstituted carbocation analogue, the extent of which will depend on the value of ρ , which is unknown.¹⁰ LFP of the *p*-isomer **3** in 9:1 H₂O–CH₃CN resulted in a very long-lived transient ($\lambda_{\max} = 350$ nm; $\tau \gg 1$ ms), consistent with the

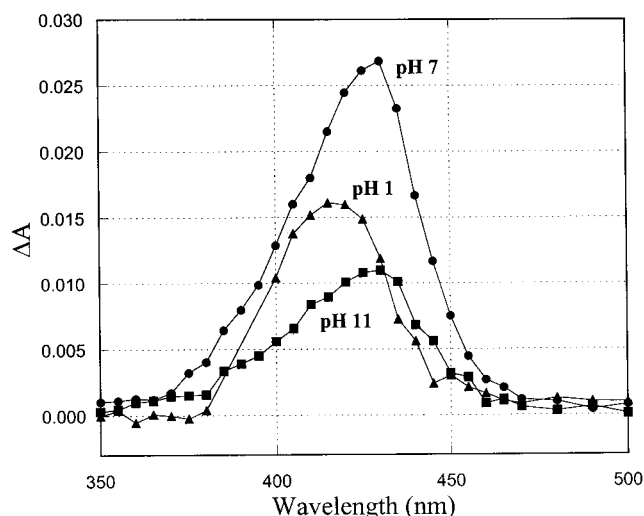
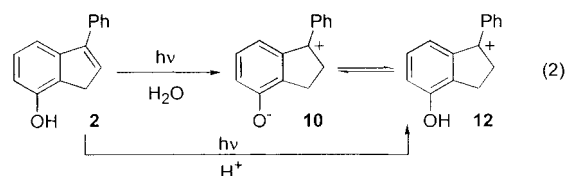


Figure 2. Absorption spectra of transients generated via LFP of **1** (or **8**) in H₂O at pH 1 (▲), 7 (●), and 11 (■), monitored ~50 ns after the laser pulse.

formation of the corresponding *p*-QM.¹⁰ For **2**, LFP in 9:1 H₂O–CH₃CN yielded a transient whose absorption ($\lambda_{\max} = 415$ nm) was similar to that of **9**. However, in this case, a sum of two first exponential decays was observed ($\tau = 4.98 \pm 0.07$ and 1.11 ± 0.02 μ s, with a 36% and 64% contribution, respectively). The absorption spectra monitored at different time intervals were the same, showing only the expected variation in intensity. This is consistent with overlapping carbocation and QM absorptions. Support for these similar QM and carbocation absorptions was provided by obtaining similar transient spectra for LFP of **2** in acidic and basic conditions. At low pH, only carbocation is expected to form, since the mechanism of acid-catalyzed photoprotonation of the double bond should dominate in acidic media, as have been observed for other aryl alkenes.^{9,11} In turn, only *m*-QM should be observable at high pH, since the hydroxy group would be deprotonated. The transient spectrum observed at pH 12 was identical to that at neutral pH, and that observed at pH 1 was blue-shifted by only ~3 nm. Also, the transient produced at high and low pH could be fitted by a single first exponential decay, indicative of the presence of only one species. These results suggest that, in neutral conditions, the two transients with lifetimes $\tau = 4.98 \pm 0.07$ and 1.11 ± 0.02 μ s can be assigned as the *m*-QM **10** and the corresponding carbocation **12**, respectively (eq 2). We propose that the initially



generated *m*-QM **10** is sufficiently long-lived for an approach to equilibrium with the carbocation **12** (requires protonation of the phenolate anion, which in neutral pH is not expected to be have a diffusion-controlled rate of protonation from water, the dominate general acid in solution). However, we do not have a full understanding of the lifetime difference of the carbocation at neutral and at low pHs; the carbocation is apparently shorter-lived (0.26 μ s) in the pH 1–3 range. This may reflect microsolvation effects which depend on the generation pathway. The potential equilibrium between the initially photogenerated QM and corresponding carbocation is not observed for **9** (or **11**)^{10b} in neutral pH since the lifetime of the initially photo-

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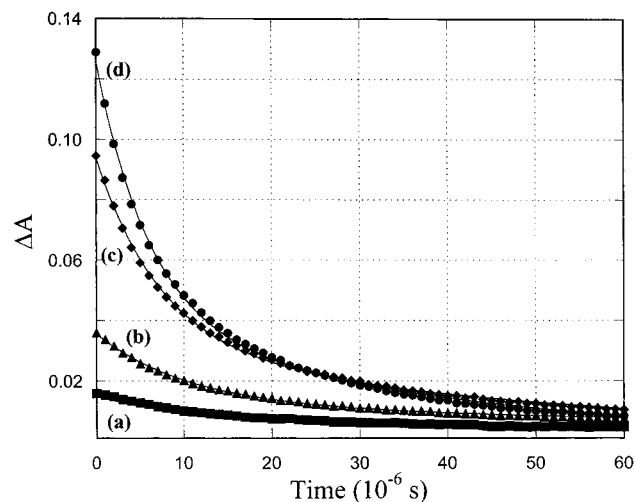


Figure 3. Decay traces of *m*-QM **10** generated via LFP of **2** at low water concentrations (in CH₃CN): (a) 0.3, (b) 0.8, (c) 1.7, and (d) 2.8 M.

generated QM (determined primarily by nucleophilic attack by water) is much shorter, preventing potential equilibration to the carbocation. LFP of **1** or **8** at pH 1 yielded a blue-shifted (~12 nm) absorption spectrum (Figure 2), attributable to the carbocation (which is now formed with higher quantum yield via *photoprotonation*) which partially decayed within the laser pulse (therefore, the amount generated at low pH is actually higher than that shown by its monitored absorbance). LFP of **1** at pH 11 yields essentially the same spectrum as that observed at pH 7, consistent with a *m*-QM intermediate (**9**) at both of these pHs (Figure 2).

Further support for our assignments made above is provided by LFP of the corresponding methoxy-substituted derivatives **4** and **5**, which did not give strongly absorbing transients as observed for **1** and **2**. In 7:3 H₂O–CH₃CN, only **5** gave a significant transient ($\lambda_{\max} = 415$ nm, $\tau = 145 \pm 4$ ns). This species has a lifetime that is significantly different from that assigned to the carbocation from **2**. With this in mind, we have assigned this transient to the radical cation of **5** since methoxy-substituted styrene derivatives have been shown to give radical cations (in LFP experiments) with pseudo-first-order decays that are insensitive to oxygen.¹³ Both **4** and **5** also gave weak absorptions at 335 nm with lifetimes of 344 ± 8 and 403 ± 2 ns, respectively, which are unassigned. It should be noted that all of these transients are significantly weaker than the transients assigned to QMs for **1–3**. The quantum yields for formation of these transients (from **4** and **5**) are probably very low since no products directly attributable to radical cations or radicals are observed in the product studies. If simple carbocations are formed from **4** and **5** (as suggested from the product studies), their transients were not readily detectable in neutral pH.

Significantly, *m*-QMs **9** and **10** were photogenerable even at low water concentrations (in CH₃CN) but not in neat CH₃CN, as shown by observation of their characteristic absorption spectra. The amount produced *increased* with *increasing water content*, and due to nucleophilic quenching by water, a concomitant decrease in lifetime was observed (Figure 3). (Lifetime traces were best fitted by a sum of two single exponentials, both of which showed the same trend in ΔA and decay with respect to water concentration, suggesting differentially solvated QMs.) Consistent with the similar diaryl ethanol

Table 1. Photophysical Parameters and Quenching Rate Constants

parameter	1	2
τ_f^a (ns)	5.6 ± 0.3	7.6 ± 0.4
Φ_f^b	0.20 ± 0.01	0.23 ± 0.02
λ_{em}^c (nm)	345	353
k_q (H ₂ O) ^d (10^8 M ⁻³ s ⁻¹)	3.1 ± 0.5	1.5 ± 0.3
k_q (D ₂ O) ^d (10^8 M ⁻³ s ⁻¹)	1.1 ± 0.1	
k_q (CH ₃ OH) ^d (10^8 M ⁻³ s ⁻¹)	0.08 ± 0.01	
K_s (M ⁻³)	0.2 ± 0.2	1.3 ± 0.2
K_d (M ⁻³)	1.7 ± 0.2	1.1 ± 0.2
τ_{QM}^e (μ s)	0.047 ± 0.001	4.98 ± 0.07^h
λ_{QM}^f (nm)	425	415
Φ_p^g	0.22 ± 0.02	0.24 ± 0.02

^a Fluorescence lifetime in neat CH₃CN as measured by single photon counting. ^b Fluorescence quantum yield in neat CH₃CN. ^c Fluorescence emission λ_{\max} . ^d Dynamic quenching rate constant ($\pm 10\%$) with H₂O, D₂O, or CH₃OH as quencher. ^e Lifetime of *m*-QM in neat H₂O for **1** and 9:1 H₂O–CH₃CN for **2**. ^f λ_{\max} of *m*-QM. ^g Photohydration quantum yield in 1:1 H₂O–CH₃CN. ^h An overlapping decay of carbocation **12** (1.11 ± 0.02) μ s was also observed.

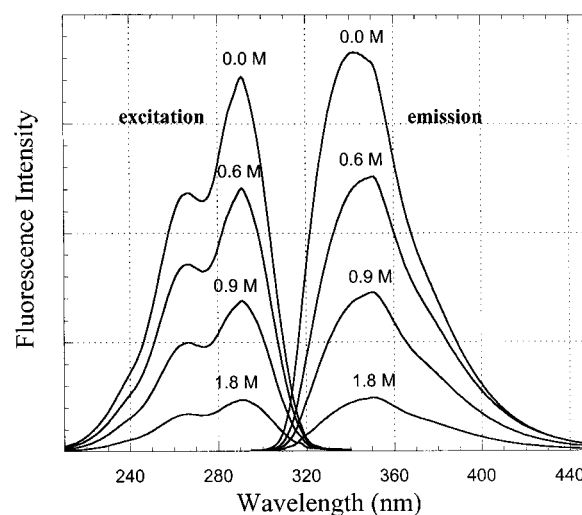


Figure 4. Representative fluorescence quenching traces of **1** by added H₂O in CH₃CN ($\lambda_{ex} = 290$ nm, $\lambda_{em} = 345$ nm).

product quantum yields (Φ_p) measured for **1** and **2**, the relative amounts of **9** and **10** produced, as measured by ΔA s in these LFP experiments, were similar (assuming **9** and **10** have similar extinction coefficients). However, **8** did not produce any *m*-QM at these low water concentrations, again suggesting that *m*-QM formation from **1** and **2** involves a more efficient process (e.g., a solvent-mediated ESIP) rather than the stepwise process proposed for hydroxy-substituted benzyl alcohols.¹⁰

Fluorescence Studies. The strong fluorescence emission bands observed for **1** and **2** (Table 1) are assigned as the normal rather than the tautomer emission based on their similarity to known aryl alkene emissions and the lack of a large Stokes shift. The emissions (Figure 4) were broad and lacked the fine structure observed in the excitation spectrum. This suggests that the molecular geometry in the excited state is less rigid than the ground state, which is consistent with a charge-transfer excited state where the alkene bond has been significantly weakened. Since Φ_f values are similar for **1** and **2**, the charge-transfer excited state is considered to have a planar structure, as indene **2** cannot twist significantly. Both **6** and **3** were very weakly fluorescent.

To gain mechanistic insight into *m*-QM formation from the excited singlet state, fluorescence quenching studies by water were carried out. Efficient quenching of the fluorescence emission of **1** and **2** by H₂O in CH₃CN was observed (~2 M

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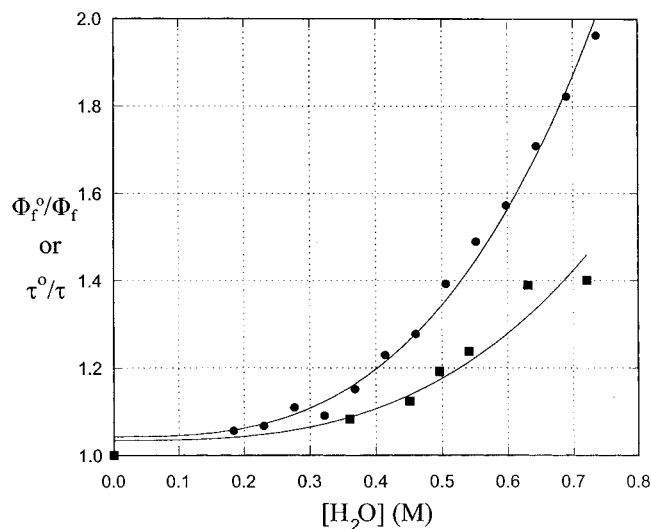


Figure 5. Stern–Volmer plots for steady-state (Φ_f^0/Φ_f , ●) and time-resolved (τ^0/τ , ■) data in the fluorescence quenching of **2** by H_2O (in CH_3CN). The lines drawn are fits to $\Phi_f^0/\Phi_f = 1 + (K_S + K_D)[\text{H}_2\text{O}]^3$ and $\tau^0/\tau = 1 + K_D[\text{H}_2\text{O}]^3$.

H_2O resulted in significant quenching) (Figure 4). Methanol quenched to a much lesser extent, while THF did not quench at all. A steady-state Stern–Volmer plot was not linear. The observed curved dependence on water (quencher) concentration has been previously observed for several other systems.^{3,4} The curved Stern–Volmer plot can be fitted to the third power in H_2O concentration (Figure 5). The high-order dependence on water concentration has been attributed to the involvement of clusters of size n during excited-state proton transfer.^{3,4} Both the steady-state and the lifetime data of **1** and **2** showed a cubed water dependence. This suggested that water in the form of a trimer was involved in the deactivation of the singlet excited state. Significantly, three water molecules would be able to span the distance between the hydroxy and alkene moieties of **1** and **2** such that the hydrogen bonds approach linearity for optimum interaction. The extent of quenching as measured by fluorescence lifetimes (τ) was significantly less than that observed from fluorescence intensities (Φ_f) (Figure 5). This difference implies that, besides the dynamic ESIPT quenching, static quenching involving weak complexation with a water trimer was occurring in the ground state. This weak complexation, however, could not be observed by UV–vis. Combining the information provided by the steady-state (eq 3) and the lifetime analyses (eq 4), static and dynamic Stern–Volmer constants (K_S and K_D ; $K_D = k_q\tau^0$) were determined (where τ^0 and Φ_f^0 denote values in the absence of quencher and k_q represents the rate constant of quenching) (Table 1).

$$\Phi_f^0/\Phi_f = (1 + K_S[\text{Q}]^3)(1 + K_D[\text{Q}]^3) \approx 1 + (K_S + K_D)[\text{Q}]^3 \quad (3)$$

$$\tau^0/\tau = 1 + K_D[\text{Q}]^3 \quad (4)$$

Dynamic quenching is more rapid for **1** than for **2**, which is consistent with **1** exerting less of a steric effect on the formation of the cyclic water trimer and substrate complex. For the dynamic quenching component of **1**, a kinetic solvent isotope effect of 2.8 was observed, which is consistent with those found for other systems involving solvent clusters in ESPTs.^{3–6}

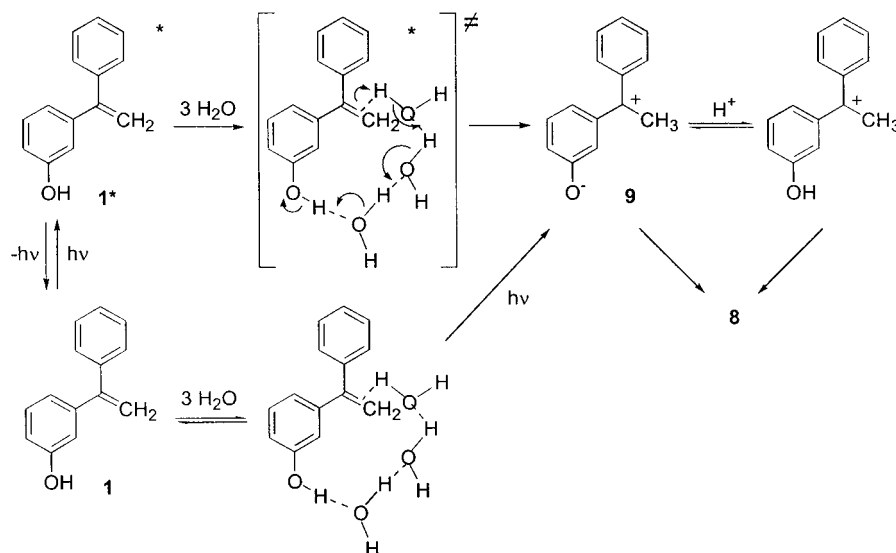
In contrast, water had a much lesser quenching effect on the fluorescence of **8** (even 100% H_2O did not cause complete quenching), which is consistent with a different mechanism of

reaction to give the same QM as from **1**. Also significant was that water had no effect on the fluorescence emissions of **4–7** at the concentrations used above or at much higher concentrations. Unfortunately, fluorescence quenching of the para isomer **3** could not be studied due to its very weak emission.

Mechanism. The following mechanism for the photohydration of **1** and **2** is proposed (Scheme 1). The excited state of **1** (or **2**) undergoes an ESIPT mediated by a water trimer cluster, giving rise to the *m*-QM, which in principle can equilibrate with the corresponding carbocation by protonation. Our data cannot distinguish between a concerted proton transfer (via a Grothuss-type mechanism) or one in which the phenolic proton is ionized to the water cluster followed by a fast reprotonation at the alkene β -carbon. Time-resolved studies using picosecond (or faster) resolution may be required in order to address the mechanism in more detail. It is clear, however, that the meta grouping of proton donor and proton acceptor does not hinder formal ESIPT, which was unexpected. The fast overall rates and high quantum efficiencies observed are further surprises. The overall ESIPT is irreversible; the *m*-QM is completely trapped by water to form the diaryl ethanol product. The mechanism is supported by the following observations. The fluorescence intensity of **1** or **2** decreased with increasing water concentration in CH_3CN , accompanied by an increase in the amount of *m*-QM produced. These effects were observed at very low water concentrations in essentially bulk CH_3CN . This is consistent with a fluorescence quenching process leading directly to *m*-QM formation. The unsubstituted and methoxy-substituted derivatives and **8** showed no fluorescence quenching at these low water concentrations, and all (with the exception of **8**) gave only very low diaryl ethanol product quantum yields. This suggests that the hydroxyl group is necessary for efficient photohydration and thus rules out a mechanism involving initial direct photoprotonation of the alkene moiety. The Stern–Volmer analyses of the fluorescence quenching of **1** and **2** revealed a cubed dependence on water concentration, which suggests the involvement of a water trimer cluster in the quenching process leading to *m*-QM formation. Association of **1** and **2** with a water trimer in the ground state was also implied. However, the low K_S values suggest that this interaction is very weak but mechanistically relevant. Direct excitation of this ground-state complex results in formation of the *m*-QM directly (probably within a few picoseconds or less), since the water molecules are already correctly arranged for ESIPT. The observation of a static component in the fluorescence quenching further strengthens our claim that the formal ESIPT is essentially concerted.

The lack of a normal fluorescence emission has been observed previously for fast proton transfers upon excitation of ground-state complexes.⁵ Any other nonspecifically solvated complexes are presumed to fluoresce like the uncomplexed form, since they first need to undergo solvent reorganization before reacting to form the *m*-QM. Indeed, the reduced quenching effect observed for methanol is consistent with involvement of a solvent cluster as the bulkier and less polar methanol is less able to mediate the proton transfer.^{3,4} Further evidence for an ESIPT pathway was provided by comparison with results for **8**, where much higher water concentrations were required for fluorescence quenching and for observable *m*-QM formation. This difference is indicative of a more efficient process operative for **1** and **2** (such as ESIPT) rather than the two-step process proposed for the hydroxy-substituted benzyl alcohols.¹⁰ Production of *m*-QM as well as that of diaryl ethanol product were diminished at high pH for both **1** and **2**, which again is consistent with an ESIPT mechanism, since if a prior adiabatic dissociation of the

Scheme 1



phenol were involved, more QM and thus more product would have been expected at high pH, as observed for the hydroxy-substituted benzyl alcohols.¹⁰

Summary. Hydroxy-substituted 1,1-diaryl alkenes **1–3** photohydrate efficiently via the corresponding QM intermediate. The results for the meta isomers are consistent with a mechanism involving water-mediated ESIPT of the phenolic proton to the β -carbon of the alkene. This ESIPT is not reversible: the QM is trapped completely by water to form the diaryl ethanol product. These systems are significant as not only can they be used as efficient new photogenerators of QM intermediates, but they can also potentially be used as probes of the dynamics of water-mediated reactions.

Experimental Section

General. ¹H NMR spectra were recorded on a Bruker AC-300 (300 MHz) instrument, and high-resolution mass spectra (HRMS) were determined with a Kratos Concept H (EI) instrument. Melting points were obtained on a Kofler hot-stage microscope and are uncorrected. Acetonitrile used for the fluorescence studies was dried over CaH₂ and distilled before use. THF and Et₂O were also dried and distilled.

Materials. The synthetic precursors 4-hydroxy-1-indanone, 4-methoxy-1-indanone, 1-indanone, 3-hydroxyacetophenone, 3-methoxyacetophenone, and 4-hydroxyacetophenone as well as **6** were purchased from Aldrich. The initial step in the preparation of compounds **1–5** was the addition of PhMgBr to the corresponding ketone in THF. Standard workup of the crude alcohol involved addition of NH₄Cl until pH \sim 9, extraction with CH₂Cl₂, drying with MgSO₄, filtration, and evaporation to dryness in vacuo.

1-*m*-Hydroxyphenyl-1-phenyl-1-ethanol (8) and *m*-Hydroxy- α -phenylstyrene (1). 3-Hydroxyacetophenone (4.0 g, 29 mmol) in THF (200 mL) was added dropwise to PhMgBr [91 mmol, prepared by adding PhBr (9.6 mL, 91 mmol) in THF (50 mL) to Mg turnings (2.3 g, 95 mmol) in THF (50 mL) and an I₂ crystal] under nitrogen in an ice bath. More THF (50 mL) had to be added since the mixture became very thick during reaction. The solution was refluxed for 3 h, and after standard workup, \sim 77% conversion to **8** was obtained. CHCl₃ was used to induce crystallization of the crude oil, and ligroines was used as the recrystallization solvent to obtain the white solid **8**: mp 113–114 °C; IR (cm⁻¹) 3570–2720; ¹H NMR (300 MHz, (CD₃)₂CO) δ 1.83 (s, 3H, CH₃), 4.55 (s, 1H, OH), 6.61 (dd, J = 8.3, 1.5 Hz, 1H, arom), 6.80–7.46 (m, 8H, arom), 8.14 (s, 1H, OH); HRMS calcd for C₁₄H₁₄O₂, 214.0994, obsd 214.0994. To obtain **1**, H₂SO_{4(aq)} (2.7 mL of 2.5 N, 10 mL of H₂O added, 6.8 mmol of H⁺) was added dropwise to crude **8** (\sim 5.8 g, \sim 21 mmol at 77%) in CH₃CN (100 mL). After refluxing for 1 h, workup (addition of saturated NaCl and 1 M NaOH until pH \sim 5,

extraction with CH₂Cl₂, drying with MgSO₄) showed an \sim 82% conversion from **8** to **1**. Purification was achieved using a silica column—an initial wash with hexanes, followed with CH₂Cl₂ to elute the oil **1**; ¹H NMR and IR data of **1** were consistent with literature data:¹⁴ IR (cm⁻¹) 3700–2940, 1610; ¹H NMR (300 MHz, CDCl₃) δ 5.04 (s, 1H, OH), 5.44 (d, J = 1.5 Hz, 1H, =CH₂), 5.45 (d, J = 1.5 Hz, 1H, =CH₂), 6.79 (m, 2H, arom), 6.93 (m, 1H, arom), 7.16–7.36 (m, 6H, arom); HRMS (EI), calcd for C₁₄H₁₂O, 196.0889, obsd 196.0887.

7-Hydroxy-3-phenylindene (2). Under nitrogen, a solution of 4-hydroxy-1-indanone (2.0 g, 13 mmol) in THF (250 mL) was added dropwise to PhMgBr [67 mmol, prepared by adding PhBr (7.1 mL, 67 mmol) in THF (100 mL) to Mg turnings (1.66 g, 68 mmol) in THF (100 mL) and refluxing for 30 min] in an ice bath. The mixture was stirred at room temperature for 1 h, refluxed for 3 h, and stirred overnight. Standard workup gave a dark emulsified solution which was first filtered before being dried with MgSO₄. The sticky crude solid contained no alcohol but rather showed a \sim 95% conversion directly to **2**. A silica column was used for purification—an initial wash with hexanes was followed by using CH₂Cl₂ to elute the white solid **2**: mp 123–124 °C; IR (cm⁻¹) 3510–3120, 1620; ¹H NMR (300 MHz, CDCl₃) δ 3.45 (d, J = 2.2 Hz, 2H, CH₂), 4.78 (s, 1H, OH), 6.57 (t, J = 2.2 Hz, 1H, =CH), 6.72 (dd, J = 6.7, 2.2 Hz, 1H, arom), 7.17–7.62 (m, 7H, arom); HRMS (EI), calcd for C₁₅H₁₂O, 208.0889, obsd 208.0886.

***p*-Hydroxy- α -phenylstyrene (3).** A solution of *p*-hydroxyacetophenone (5.0 g, 37 mmol) in THF (250 mL) was added dropwise to PhMgBr [0.21 mol, prepared by adding PhBr (22 mL, 0.21 mol) in THF (50 mL) to Mg turnings (5.0 g, 0.21 mol) in THF (50 mL) and an I₂ crystal] in an ice bath. After the solution was stirred for 30 min, the reaction was complete, and standard workup yielded \sim 97% of alcohol. A few grains of *p*-toluenesulfonic acid were added to the crude alcohol (\sim 0.5 g, \sim 2.3 mmol) in toluene (100 mL), followed by a 1 h reflux. Standard workup afforded the oil **3** (98%); ¹H NMR data of **3** were consistent with literature data:¹⁵ IR (cm⁻¹) 3700–2800, 1610; ¹H NMR (300 MHz, CDCl₃) δ 4.97 (s, 1H, OH), 5.34 (d, J = 1.4 Hz, 1H, =CH₂), 5.38 (d, J = 1.4 Hz, 1H, =CH₂), 6.78 (d, J = 8.6 Hz, 2H, arom), 7.19–7.35 (m, 7H, arom); HRMS (EI), calcd for C₁₄H₁₂O, 196.0889, obsd 196.0885.

***m*-Methoxy- α -phenylstyrene (4).** 3-Methoxyacetophenone (2.0 g, 13 mmol) in THF (100 mL) was added dropwise to PhMgBr (20 mL of 1 M Aldrich solution, 20 mmol) under nitrogen in an ice bath. The solution was stirred for 1 h at room temperature, heated at \sim 45 °C for

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1 h, and stirred overnight, followed by standard workup. The reaction was not pushed to completion since several side products formed. $\text{H}_2\text{SO}_{4(\text{aq})}$ (5 mL of 50%, 90 mmol H^+) was added to the above crude mixture in CH_3CN (50 mL). Refluxing this solution for 3 h, followed by workup (extraction with CH_2Cl_2 and drying with MgSO_4), afforded a relatively clean reaction mixture of ~43% **4** and ~57% of starting ketone. For purification, a silica column was used—an initial wash with hexanes, followed by 2:8 CH_2Cl_2 –hexanes to elute the oil **4**: ^1H NMR and IR data of **4** were consistent with literature data;¹⁶ IR (cm^{-1}) 1600; ^1H NMR (300 MHz, CDCl_3) δ 3.78 (s, 3H, OCH_3), 5.45 (s, 2H, $=\text{CH}_2$), 6.83–6.95 (m, 3H, arom); 7.20–7.38 (m, 6H, arom); HRMS (EI), calcd for $\text{C}_{15}\text{H}_{14}\text{O}$, 210.1045, obsd 210.1044.

7-Methoxy-3-phenylindene (5). 4-Methoxy-1-indanone (0.5 g, 3 mmol) dissolved in THF (60 mL) was added dropwise to PhMgBr (10 mL of 1 M Aldrich solution, 10 mmol). The solution was stirred for 30 min and heated at 40–50 °C for 2 h. Standard workup showed an ~85% conversion directly to **5** with 15% ketone remaining. A silica column with hexanes as eluant was used to isolate the oil **5**: IR (cm^{-1}) 1610; ^1H NMR (300 MHz, CDCl_3) δ 3.47 (d, $J = 2.2$ Hz, 2H, CH_2), 3.93 (s, 3H, OCH_3), 6.58 (t, $J = 2.2$ Hz, 1H, $=\text{CH}$), 6.81 (d, $J = 8.2$ Hz, 1H, arom), 7.21–7.63 (m, 7H, arom); HRMS (EI), calcd for $\text{C}_{16}\text{H}_{14}\text{O}$, 222.1045, obsd 222.1042.

3-Phenylindene (7). Following a procedure similar to one reported previously,¹⁷ PhMgBr (98 mL of 1 M Aldrich solution, 98 mmol) in Et_2O (200 mL) was added dropwise to 1-indanone (10.0 g, 75.7 mmol) in Et_2O (100 mL) in an ice bath, resulting in a milky white solution. After the solution was stirred at room temperature for 3.5 h, saturated NH_4Cl (70 mL) was added slowly, turning the solution a clear yellow color. The ether layer was decanted, filtered, and dried with Na_2SO_4 , and the solvent was removed in vacuo, resulting in ~38% **7** and ~57% alcohol with 5% ketone remaining. To a solution of this crude mixture (2.0 g) in CH_3CN (100 mL), $\text{H}_2\text{SO}_{4(\text{aq})}$ (10 mL of 5%, 18 mmol H^+) was added. After heating of the mixture for 1.5 h at 40–50 °C in a water bath, stirring overnight, and workup (saturated NaCl , extraction with CH_2Cl_2 , drying with MgSO_4), complete conversion of alcohol to **7** occurred. Purification was achieved using a silica column with hexanes as eluant: the ^1H NMR data of **7** were consistent with literature data;¹⁸ IR (cm^{-1}) 1600; ^1H NMR (300 MHz, CDCl_3) δ 3.51 (d, $J = 2.2$ Hz, 2H, CH_2), 6.58 (t, $J = 2.2$ Hz, 1H, $=\text{CH}$), 7.22–7.64 (m, 9H, arom); HRMS (EI), calcd for $\text{C}_{15}\text{H}_{12}$, 192.0940, obsd 192.0935.

Product Studies. A solution of ~ 10^{-3} M compound was poured into a quartz vessel with a cooling finger and purged with argon for approximately 15 min before and continuously during irradiation in a Rayonet RPR 100 photochemical reactor using 254-nm lamps (16 lamps were used unless otherwise stated). The solution was saturated with NaCl , extracted with CH_2Cl_2 , and dried with MgSO_4 . The same procedure was followed for the control, except the argon purge and the irradiation step were omitted. ^1H NMR was used to calculate the percentage conversion. Isolation of the diaryl ethanol product proved to be problematic due to its lability on the silica preparative TLC (conversion back to the diaryl alkene occurred). Therefore, only partial ^1H NMR is reported, giving the distinguishable shifts characteristic of the alcohol product in the mixture with the alkene starting material.

Photolysis of 1. A 25-mg sample was irradiated for 2 min (8 lamps) in 1:1 H_2O – CH_3CN (100 mL), yielding 25% of **8**. The identity of the product was based on its distinct ^1H NMR peaks within the mixture, being characteristic of those of **8** synthesized previously. Repeating the above using an irradiation time of 5 min (16 lamps) resulted in clean conversion to 94% of **8**. The photosolvolysis intermediate of **1** can also be trapped by CH_3OH —irradiation for 5 min (16 lamps) in 1:1 H_2O – CH_3OH gave 76% methyl ether product [^1H NMR (partial) (300 MHz, CDCl_3) δ 1.83 (s, 3H, CH_3), 3.15 (s, 3H, OCH_3)] and 22% of **8** with 2% of **1** remaining.

Photolysis of 2. A 25-mg sample dissolved in 30 mL of D_2O – CH_3CN was irradiated for 30 min, resulting in 82% conversion to **2**

deuterated at position 2. The percent conversion was determined from the decrease in area of the proton at position 2, due to deuterium incorporation. The relative intensities of MS (CI) of the mixture [m/z 209 ($\text{M}^+ + 1$, **2**) and 210 ($\text{M}^+ + 1$, deuterated **2**)] suggested 76% conversion. A 25-mg sample dissolved in 1% D_2O (0.55 M) in CH_3CN and irradiated for 4 min (16 lamps) yielded a 36% conversion. Increasing the irradiation time to 15 min (8 lamps) gave a 60% conversion. The expected diaryl ethanol 4-hydroxy-1-phenyl-1-indanol (12% and 28%) was produced upon irradiation (25 and 75 min) of a 10-mg sample dissolved in 3 mL of D_2O – CD_3CN in an ^1H NMR tube: ^1H NMR (partial) (300 MHz, CDCl_3) δ 2.34 (m, 1H, CH_2), 2.76 (m, 1H, CH_2), 2.94 (m, 1H, CH_2), 6.49 (d, $J = 7.7$ Hz, 1H, arom), 6.70 (d, $J = 8.1$ Hz, 1H, arom). Upon the addition of acid in excess D_2O to the mixture containing 28% product, complete elimination to deuterated **2** occurred (25%). In acid, **2** was found to be thermally labile—a 5.5-mg sample was dissolved in 0.8 mL of CD_3CN and 1 drop of concentrated D_2SO_4 , upon which 63% of deuterated **2** was observed.

Photolysis of 3. A 25-mg sample dissolved in H_2O – CH_3CN (100 mL) was irradiated (2 min, 8 lamps), yielding 9% 1-*p*-hydroxyphenyl-1-phenyl-1-ethanol: ^1H NMR (partial) (300 MHz, CDCl_3) δ 1.86 (s, 3H, CH_3). Increasing the irradiation time to 10 min resulted in 38%.

Photolysis of 4. A 26.3-mg sample dissolved in 1:1 H_2O – CH_3CN was irradiated for 10 min (8 lamps), resulting in 8% conversion to 1-*m*-methoxyphenyl-1-phenyl-1-ethanol: ^1H NMR (partial) (300 MHz, CDCl_3) δ 1.93 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.77 (dd, $J = 8.8$, 2.9 Hz, 1H, arom). Upon increasing the irradiation time to 30 min (16 lamps), a 25-mg sample resulted in 44% conversion.

Photolysis of 7. Only after 1 h of irradiation did a 25-mg sample in H_2O – CH_3CN (100 mL) yield 10% 1-phenyl-1-indanol as product: ^1H NMR (partial) (300 MHz, CDCl_3) δ 2.49 (m, 1H, CH_2), 2.71 (m, 1H, CH_2), 2.95 (m, 1H, CH_2), 3.16 (m, 1H, CH_2). Increasing the irradiation time to 2 h resulted in 32% alcohol product.

Quantum Yields. Product quantum yields (Φ_p) for **1** and **2** were determined using an Oriel 200-W Hg arc lamp and an Applied Physics monochromator set for 254 nm. Potassium ferrioxalate¹⁹ was used as the chemical actinometer. UV–vis spectroscopy was used to monitor for the extent of photohydration of **1** and **2** ($\epsilon = 2.20 \pm 0.08$) $\times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ at 290 nm; **2**, $\epsilon = (1.84 \pm 0.05) \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ at 300 nm). Solutions of **1** and **2** (~ 10^{-3} M) in H_2O – CH_3CN were irradiated for 5 min in UV–vis cuvettes (conversion ~10%). Both the standard and sample solutions were purged with argon 10 min before and during irradiation in order to eliminate oxygen and ensure a mixed solution. Only relative quantum yields were determined for **3** and **4**. A relative quantum yield study vs pH was carried out by monitoring the absorbance change at λ_{max} (loss in absorbance kept below 25%). Solutions of ~ 10^{-3} M **1** or **2** in 9:1 H_2O – CH_3CN at a specific pH were purged for 5–10 min with argon prior to irradiation (2–4 min) in a Rayonet RPR 100 photochemical reactor with eight lamps at 254 nm using a merry-go-round.

The UV–vis traces for photohydration of **2** in 1:1 H_2O – CH_3CN (Figure 1) were obtained in the following manner. A 3.7-mg sample of **2** in 3 mL of H_2O – CH_3CN was purged with argon for 5 min, and then a 0.1-mL aliquot was removed, diluted to 3 mL with H_2O – CH_3CN , and its absorption spectrum taken. The remaining concentrated solution was purged again for 5 min, irradiated for 5 min at 254 nm (8 lamps), and its absorption spectrum taken (again by removing a 0.1-mL aliquot), and this process was repeated until a total of 30 min irradiation time.

Laser Flash Photolysis (LFP). All transient spectra and lifetimes were obtained using a Nd:YAG laser (Spectra Physics Quanta-Ray, GCR, <30 mJ) with pulse width of ~10 ns and excitation wavelength of 266 nm. Flow cells were used, and solutions were purged with oxygen for approximately 10 min before excitation. Optical densities at 266 nm were kept below 0.3, ensuring substrate concentrations $\leq 10^{-5}$ M. No significant differences were observed in LFP runs carried out in aqueous solution under N_2 or O_2 purging, indicating that T–T absorptions are insignificant in our LFP data.

Steady-State and Time-Resolved Fluorescence Measurements. All solutions (absorbance ~0.1 at $\lambda_{\text{ex}} = 290$ nm (except 300 nm for **3**

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and 275 nm for **8**) were purged with argon for 10 min before analysis. Steady-state fluorescence spectra were obtained using a Photon Technology International A-1010 (PTI) Quanta-Master luminescence spectrometer. Fluorescence quantum yields (Φ_f) in CH₃CN were determined by comparing the integrated emission bands of **1** and **2** with that of 2-aminopyridine in 0.05 M H₂SO₄ and correcting for differences in the refractive index.²⁰ The fluorescence lifetimes were

measured on a PTI LS-1 instrument using the time-correlated single-photon-counting technique (5000 or 10 000 counts).

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