THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

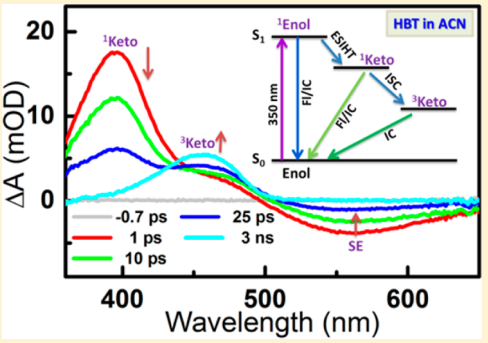
Solvent-Dependent Excited-State Hydrogen Transfer and Intersystem Crossing in 2-(2′-Hydroxyphenyl)-Benzothiazole

Shawkat M. Aly,† Anwar Usman, Maytham AlZayer, Ghada A. Hamdi, Erkki Alarousu, and Omar F. Mohammed*

Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

Supporting Information

ABSTRACT: The excited-state intramolecular hydrogen transfer (ESIHT) of 2-(2′-hydroxyphenyl) benzothiazole (HBT) has been investigated in a series of nonpolar, polar aprotic, and polar protic solvents. A variety of state-of-the-art experimental methods were employed, including femto- and nanosecond transient absorption and fluorescence upconversion spectroscopy with broadband capabilities. We show that the dynamics and mechanism of ESIHT of the singlet excited HBT are strongly solvent-dependent. In nonpolar solvents, the data demonstrate that HBT molecules adopt a closed form stabilized by O−H···N chelated hydrogen bonds with no twisting angle, and the photoinduced H transfer occurs within 120 fs, leading to the formation of a keto tautomer. In polar solvents, owing to dipole−dipole cross talk and hydrogen bonding interactions, the H transfer process is followed by ultrafast nonradiative deactivation channels, including ultrafast internal conversion (IC) and intersystem crossing (ISC). This is likely to be driven by the twisting motion around the C−C bond between the hydroxyphenyl and thiazole moieties, facilitating the IC back to the enol ground state or to the keto triplet state. In addition, our femtosecond time-resolved fluorescence experiments indicate, for the first time, that the lifetime of the enol form in ACN is approximately 280 fs. This observation indicates that the solvent plays a crucial role in breaking the H bond and deactivating the excited state of the HBT. Interestingly, the broadband transient absorption and fluorescence up-conversion data clearly demonstrate that the intermolecular proton transfer from the excited HBT to the DMSO solvent is about 190 fs, forming the HBT anion excited state.



1. INTRODUCTION

Over the past three decades, excited-state intramolecular hydrogen transfer (ESIHT) has been intensively studied to gain insight into the mechanism of the transfer process and the accompanying intramolecular rearrangements.[1−10] Despite the progress in the field of ESIHT, until now, most studies have been performed in nonpolar solvents, guaranteeing that the reaction coordinate is intact during the electronic excitation, and all excited molecules are released on the same region of the excited-state energy surface. However, extensions of the studies of ESIHT into polar solvents have been limited, partly because these experiments result in a distribution of conformations with hydrogen bonding to the solvent competing with the intramolecular hydrogen bond. More specifically, electronic excitation of such an ensemble with a broad distribution of conformations may lead to multiple starting conditions in the excited-state energy surface. Additionally, polar solvation may strongly affect the ESIHT process, resulting in different outcomes for the reaction dynamics in terms of reaction yields and reaction pathways. Monitoring the excited-state relaxations of such systems in this regime using ultrafast time-resolved vibrational, absorption, and fluorescence spectroscopies is vital to deciphering the ESIHT process in a variety of molecules in many chemical and biological systems.[8,11−15]

Among the potential ESIHT molecules, HBT (2-(2′-hydroxyphenyl)-benzothiazole),[16−18] HBO (2-(2′-hydroxyphenyl)benzoxazole),[19] 10-HBQ (10-hydroxybenzo[h]-quinoline),[20] and HBA (2-hydroxy-benzaldehyde)[21] are four prototypes for single H transfer where the enol−keto tautomerization process is the photoinduced reaction pathway. Typically, right after optical excitation, redistribution of electronic charge induces skeletal deformations and changes in the acidity and basicity of the H donor and acceptor moieties, respectively, leading to a motion of the H from the donor to the acceptor on a time scale of less than 60 fs.[22−26] In particular, the ground-state HBT in nonpolar solvent is stabilized by an O−H···N intramolecular hydrogen bond between the hydroxyphenyl and benzothiazole moieties,

Special Issue: Photoinduced Proton Transfer in Chemistry and Biology Symposium

Received: August 30, 2014
Revised: October 15, 2014

   dx.doi.org/10.1021/jp508777h | J. Phys. Chem. B XXXX, XXX, XXX−XXX

forming a closed form of cis−enol tautomer.[17,27,28] It is worth noting that the ESIHT in this condensed phase causes a substantial structural rearrangement attributed to the keto tautomer formation, which is indicated by a new vibrational band at 1600 cm^{-1}, attributed to the C═O stretching mode, and a fluorescence Stokes shift of approximately 10 000 cm^{-1}.[25,27,29] Recently, it has been reported that the torsional motion is crucial for the excited chromophore to cross a conical intersection between the excited and ground states, and the internal conversion has been considered to be a key element in the excited-state deactivation of ESIHT molecules.[28,30−32]

In this study, we explore the excited-state dynamics of HBT in a series of nonpolar, polar aprotic, and polar protic solvents using a combination of various state-of-the-art experimental techniques. The femtosecond time-resolved data clearly show not only that the conformation of the HBT in the excited state is substantially different in the polar solvent compared with the nonpolar ones but also that internal conversion (IC) and intersystem crossing (ISC) are the main deactivation pathways of the HBT excited state. Furthermore, ground-state and intermolecular proton transfer to the solvent has also been observed and confirmed via an independent experiment in a basic solution. The broadband fluorescence up-conversion data clearly demonstrate that the intermolecular proton transfer from the excited HBT to the DMSO solvent is about 190 fs, forming the HBT anion excited-state species.

It is worth pointing out that there are several reports on the ultrafast photophysics of HBT mainly in nonpolar solvents and recently in ACN.[4,33,34] In the present contribution, we provided for the first time clear evidence for the ultrafast intermolecular proton transfer from HBT to DMSO. In addition, to the best of our knowledge, this is the first detailed report of singlet- and triplet-state photophysics of HBT in a variety of polar and nonpolar solvents from fs to μs time scales using a combination of time-resolved absorption and fluorescence spectroscopy with broadband capabilities.

2. METHODS

Materials. The HBT (97% purity) and solvents (tetrachloroethylene, TCE, acetonitrile, ACN, methanol, MeOH, and ultrapure dimethyl sulfoxide, DMSO ≥99.9%) in spectroscopic grade were purchased from Sigma-Aldrich and used without further purification. For the steady-state and time-resolved absorption, the concentration of HBT was 2 mM, while diluted solutions of 10 μM were used for the steady-state fluorescence measurements.

Instrumentation for Steady-State Characterization. Steady-state absorption and fluorescence spectroscopies were used to characterize the HBT structure in the ground state. A Cary 5000 UV−visible spectrometer (Agilent Technologies) was used for absorption measurements, and a FluoroMax-4 spectrofluorometer (Horiba Scientific; slit width of 5 nm and scan rate of 500 nm/min) was used to record the fluorescence spectra after excitation at 330 nm.

Instrumentation for fs and ns TA Spectroscopy. Pump−probe fs TA spectroscopy was performed on Helios and EOS spectrometers; the experimental setup of the transient absorption has been previously reported in detail.[15,35] Briefly, we applied two laser beams; a white-light continuum probe pulse generated using a CaF_2 crystal and a spectrally tunable (240−2600 nm) 35 fs pump pulse with an energy of 25 μJ generated in an optical parametric amplifier (Newport Spectra-Physics). In this particular experiment, the pump pulses are centered at 350 nm where S_0−S_1 transition of HBT is located. The pump and probe pulses overlapped in a 2 mm thick cuvette cell containing the solutions of HBT, and the absorbance change (ΔA) in the probe pulse was successfully monitored using a broadband UV−vis detector. The sample solutions were constantly stirred during the experiments using a magnetic stirrer to make fresh solution available for each laser shot. To cover the transient spectra from fs to μs time scales after photoexcitation, we employed two detection systems, namely, a Helios and an EOS, with time resolutions of 120 fs and 1 ns, respectively. The detection limits of the two systems are 5.5 ns and 1 ms, respectively. All TA experiments were performed at room temperature.

Fluorescence Upconversion Spectroscopy. Fluorescence upconversion measurements were performed on a Halcyone MC multichannel detector with a temporal resolution of 60 fs, and the experimental setup is detailed elsewhere.[36] Briefly, a 2 mm thick cuvette containing a solution of HBT in various solvents—TCE, ACN, MeOH, and DMSO—was excited with 350 or 420 nm light from a Ti:sapphire femtosecond regenerative amplifier operating at 800 nm with 35 fs pulses. The fundamental pulse was used as a gate pulse for the up-conversion process. Then, the sample fluorescence was mixed with the gate pulses in a nonlinear crystal (BBO) and the sum-frequency signal was detected by a photon-counting method.

3. RESULTS AND DISCUSSION

Steady-State Absorption and Emission of HBT in Different Solvents. The absorption and emission spectra of HBT in TCE, ACN, MeOH, and DMSO are located in the near-UV and visible regions (see Figure 1). The first absorption band peaks at around 338 nm in nonpolar media and at 331 in ACN and MeOH. This absorption band has been assigned to the S_0−S_1 ($\pi\pi^*$) transition of the neutral cis−enol tautomer (zero twisting angle around the central C−C bond between the hydroxyphenyl and benzothiazole moieties) with an extinction coefficient of 1.26×10^4 M^{-1} cm^{-1}.[18,27] The bathochromic spectral shift in nonpolar solvents with respect to the polar solvents can be explained by the fact that, in TCE, HBT forms a strong intramolecular hydrogen bond in the enol ground-state configuration, elongating or enhancing π-electron delocalization along the H-chelate bond. A similar spectral shift was observed in other intramolecular hydrogen transfer systems.[37]

As can be seen in Figure 1, HBT behaves differently in DMSO compared with other solvents. More specifically, in addition to the neutral cis−enol tautomer band, a broad absorption band at 427 nm is observed. This band can be attributed to the HBT anion due to partly ground-state proton transfer to the solvent. This interpretation is confirmed experimentally by dissolving the HBT in DMSO with an addition of a small amount of NaOH, which gives the anion spectrum at the same wavelength position (see Figure 1; lower panel).

Upon optical excitation at 330 nm, nearly resonant with the S_0−S_1 transition, the emission spectrum in the nonpolar TCE shows a single peak at 550 nm. The large Stokes shift indicates that the excited closed-form enol tautomer transformed into the planar, closed-form keto HBT.[9,10] In contrast, in the polar solvents, the emission spectra show two peaks at 378 and 540 nm in MeOH and 366 and 510 in ACN. These results clearly indicate that the conformations of the excited HBT are different in the polar and nonpolar solvents. It should be noted

dx.doi.org/10.1021/jp508777h | J. Phys. Chem. B XXXX, XXX, XXX−XXX

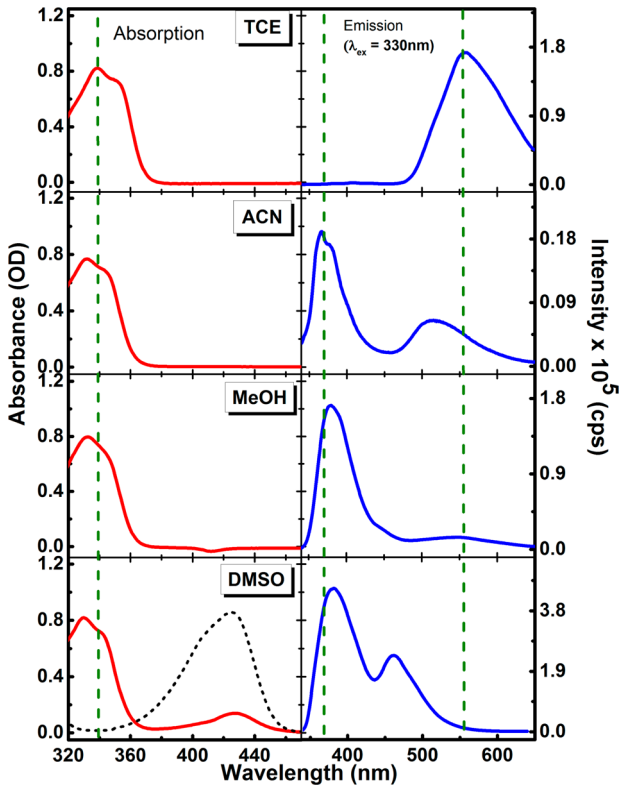


Figure 1. Absorption and emission spectra of HBT after 330 nm excitation in TCE, ACN, MeOH, and DMSO. The dashed line in the bottom panel is the absorption spectrum of HBT in NaOH solution.

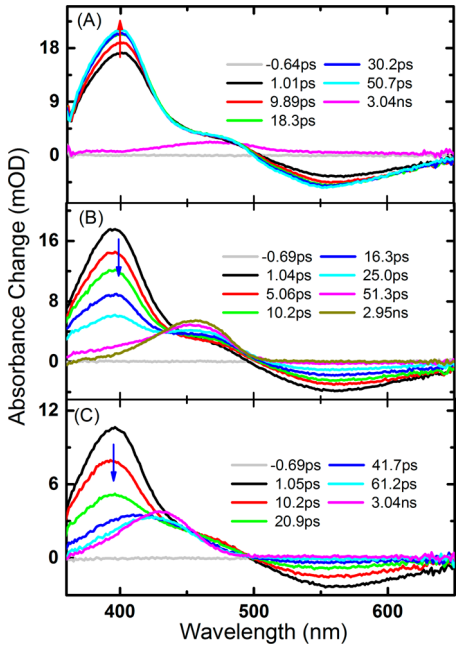


Figure 2. TA spectra of HBT dissolved in TCE (A), ACN (B), and in MeOH (C) at different time delays from −0.7 to 3 ns after 350 nm photoexcitation.

that the intramolecular H-bond in HBT can be disturbed when HBT is dissolved in polar solvents like MeOH or DMSO. In this situation, the intramolecular H-bond may be replaced by intermolecular H-bonds involving solvent molecules. Consequently, the C−C bond between the hydroxyphenyl and thiazole moieties can be twisted, resulting in multiple HBT conformations in the ground state.[9] Since the twisting does not induce a large change in the π-conjugation of the molecule, the absorption spectral shape and peak of planar and nonplanar structures should not be very different. The multiple HBT configurations in the polar solvents may lead to different isomers of the excited HBT, resulting in different fluorescence spectra, where the large Stokes shift can be attributed to the enol-to-keto tautomerization of HBT and the short Stokes shift can be attributed to the excited enol tautomer, which is not able to undergo H transfer. This finding demonstrates that conformations HBT in the excited are controlled by the polarity and hydrogen bonding capability of the solvent. Interestingly, the fluorescence intensity in ACN is a factor of approximately 30 times less than that in TCE, which indicates that in the polar solvent, the radiationless deactivation mechanisms becomes much more effective. This observation is in agreement with the S_1 lifetimes of HBT, which are 300 ps in TCE and 14 ps in ACN.[16] In contrast, in solvents with a high polarity and proton accepting capability, such as DMSO, the HBT emission has two peaks at 380 and 460 nm, which may be related to the existence of two electronic states that can be attributed to the neutral enol tautomer and the HBT anion in the excited state. This observation provides an indication of the absence of intramolecular hydrogen transfer and the formation of the keto tautomer, which was confirmed by performing the experiments in a basic solution, guaranteeing that HBT exists completely in the anionic form.

Hydrogen Transfer in Nonpolar Solutions. In Figure 2, we present time-dependent ΔA spectra from −0.7 ps to 3 ns after 350 nm laser excitation. The TA spectra show the sum of the excited singlet-state absorption (ESA; around 400 nm) and the stimulated emission (SE; at around 550 nm, in ACN), while ground-state bleach below 400 nm is not observed due to the strong spectral overlap with the excited-state absorption of the keto form. The formation of the excited-state absorption and the stimulated emission of the keto within our time resolution (120 fs) provide clear evidence that the H transfer is indeed ultrafast. As can be clearly seen in Figure 2, the ESA band of the keto tautomer is formed right after excitation in TCE, and this is followed by an additional rise (due to vibrational cooling) with a characteristic time constant of 9.4 ps. Being in this regime, such a cooling process of the excited-state molecules toward ambient temperature leads to band narrowing (see Figure S1, Supporting Information). This observation is in good agreement with the time-resolved IR data reported by Nibbering and co-workers.[9,38] In this case, the photoexcitation takes place via a vertical transition, maintaining the nuclear configuration of the molecules during the excitation. In this regime, quantum chemical calculations indicate that the electron density on the N of the thiazole moiety is increased, whereas the O−H covalent bond is weakened.[33] Thus, immediately after optical excitation, a redistribution of the electronic charge takes place, modifying the bond lengths, hydrogen bond distance, and donor−acceptor strength, and a new potential surface for the hydrogen bond is formed. As shown in Figure 4, the decay of the excited HBT keto state fits with a single exponential with characteristic time constants of 329.5 in TCE, which is in good agreement with the reported lifetimes of HBT in TCE (300 ps).[16,27] Interestingly, the decay of the ESA band is accompanied by the appearance of a new

dx.doi.org/10.1021/jp508777h | J. Phys. Chem. B XXXX, XXX, XXX−XXX

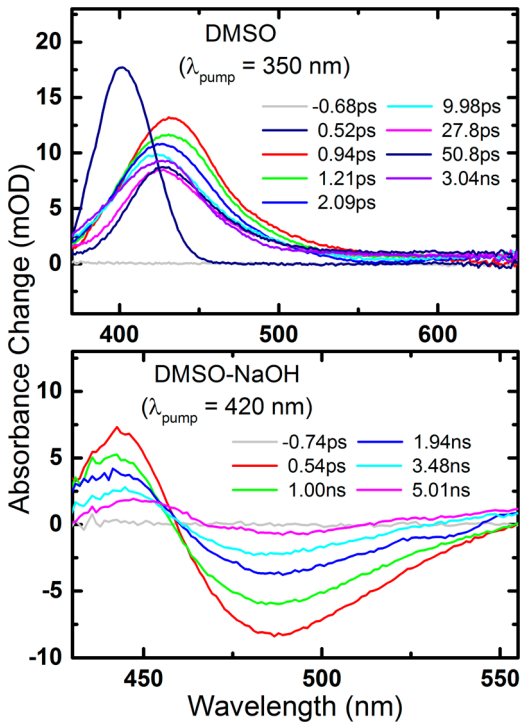


Figure 3. TA spectra of HBT dissolved in DMSO and DMSO/NaOH (as indicated) at different time delays from −0.7 to 3 ns; excitation wavelengths are indicated in the figure.

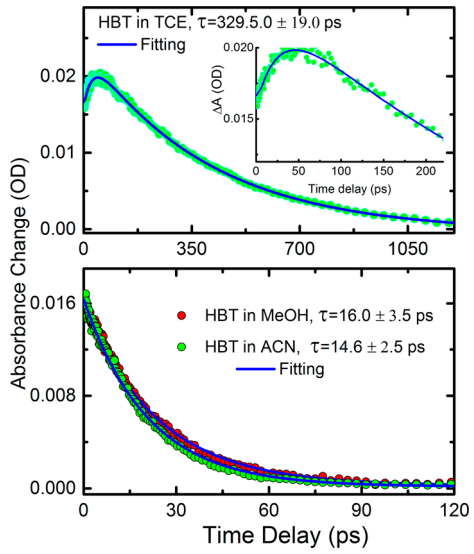


Figure 4. Kinetics of the TA spectra at 400 nm for HBT in TCE (top panel, inset: short time range), ACN, and MeOH (lower panel).

and long-lived spectral feature located at 460 nm. This component has a long lifetime, longer than the detection limit of our machine. On the basis of the lifetime, this long-lived species can be attributed to triplet−triplet absorption resulting from ISC, as discussed below.

Hydrogen Transfer in Polar Solvents. The ΔA spectra in ACN and MeOH are presented in Figure 2. In MeOH and ACN, the ESA band is rapidly developed within the time resolution, and it decays with a time constant of tens of picoseconds. This result has been confirmed by conducting fs time-resolved fluorescence experiments, which show that the formation of the keto emission is ultrafast (see Figure 5). In

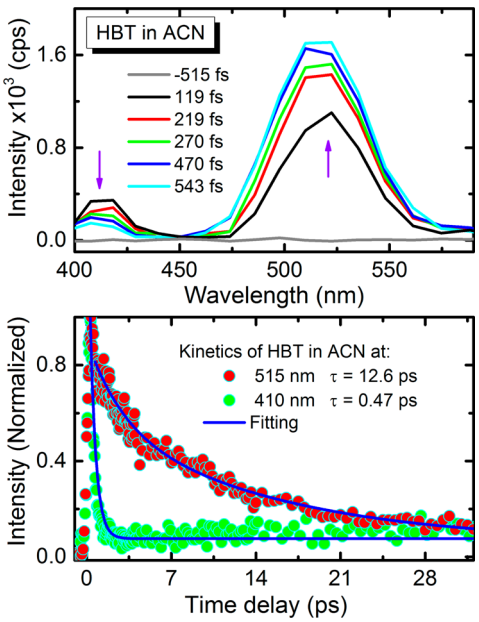


Figure 5. Broadband fluorescence spectra of HBT in ACN (top) and kinetics collected at different wavelengths (bottom) as indicated in the figure.

addition, the fs time-resolved fluorescence data also indicate that the lifetime of the enol form in ACN is less than 500 fs (see Figure 5). As can be seen in Figure 2, the decay of the ESA is followed by the rise of a new excited absorption at 460 nm, which decays in the μs regime, and can also be attributed to the triplet−triplet absorption.

Unlike the HBT in TCE, where a strong intramolecular hydrogen bond formed making a closed form and maintaining coplanarity in the HBT molecule, the H bond of HBT is strongly disturbed in the polar solvents, resulting in different deactivation pathways for the excited state. One possible scenario is that, as a result of weakening or breaking the H bond, the keto tautomer may be twisted around the central C−C bond. This twisting motion can drive the system to a conical intersection between the excited state and the ground state, leading to an ultrafast IC to the ground state. It is well reported that this type of torsional motion around the C−C bond can play an important role in the deactivation mechanisms of the excited state of many other organic molecules such as stilbene or azobenzene.[39−42] Specifically, the significant role of this twisting motion on the IC of HBT was reported by Barbara et al.,[28] and very recently, the quantum chemical calculation of HBT has clearly demonstrated that an S_0/S_1 conical intersection with a 90° twisted structure exists and is responsible for the ultrafast IC.[32]

In DMSO, on the other hand, the ring opening process is followed by proton transfer from the excited enol form to the solvent media, which may also lead to the population of the twisted anion form, resulting in equilibrium with the twisted enol form. The growth rate of the anion is clearly shown in Figure 3. The strong spectral overlap of the enol tautomer and anion form of HBT hamper the precise determination of the growth rate of the anion form. However, with the fluorescence upconversion experiments, we are able to accurately resolve such a process. More specifically, the data indicate that the transition from the enol to anion form is ultrafast, ∼200 fs (see Figure 7).

dx.doi.org/10.1021/jp508777h | J. Phys. Chem. B XXXX, XXX, XXX−XXX

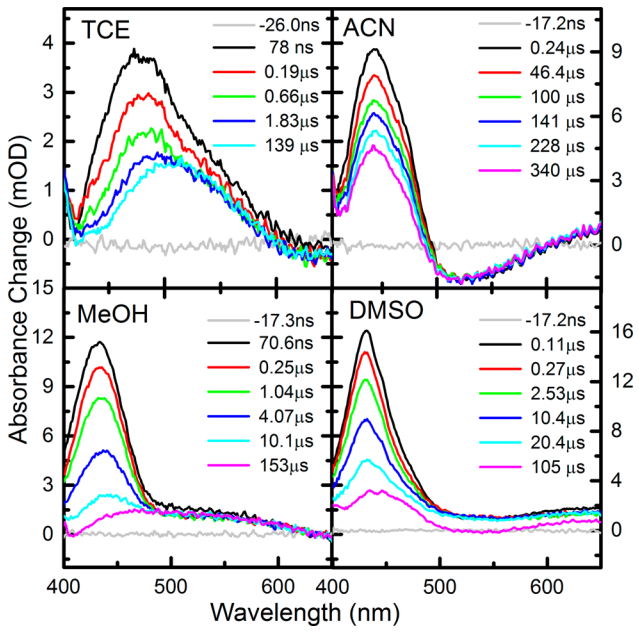


Figure 6. ns-TA spectra of HBT dissolved in TCE, ACN, MeOH, and DMSO (as indicated) in ns to μs time delays after 350 nm photoexcitation.

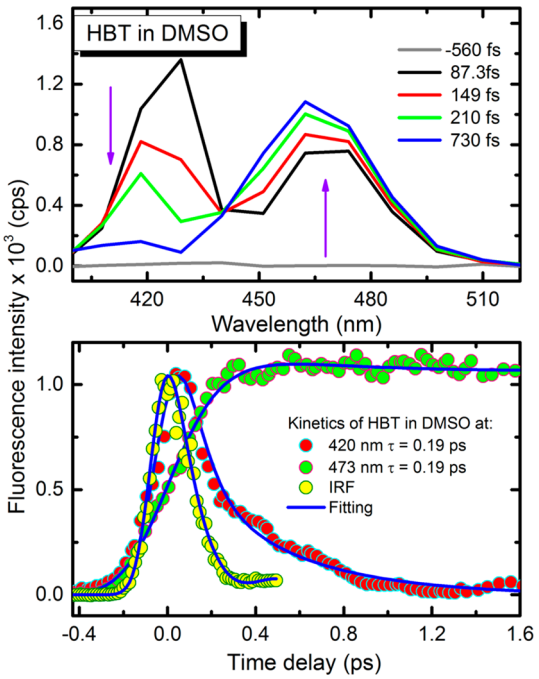


Figure 7. Fluorescence upconversion spectra of HBT in DMSO (top) and kinetics collected at different wavelengths (bottom) as indicated in the figure. The IRF is also inserted in the figure.

It is well established that there is a direct relation between the photoacidity of the molecules (represented by pK_a*) and the rate of the proton transfer.[43] In the ground state, the pK_a value of HBT in water is approximately 10.2−10.4,[44−46] suggesting that HBT is a poor acid in the ground state. On the other hand, the pK_a* of HBT in the excited state is 1.3,[45] which is much smaller than that in the ground state. With such a level of pK_a*, HBT* can be considered as an intermediate-strength photoacid, not a superphotoacid which assists the ESPT by lowering the height and width of the potential barrier leading to the ESPT time constant of a few hundreds fs.[43] However, we have to consider that the ESPT rate may also be determined by the basicity of the solvent media. In other words, the intermolecular acid−base interaction may lower the energy barrier with respect to the proton transfer. In this regard, we note that pK_a of DMSO is 35.1, much higher than those of other solvents used in this study; for instance, pK_a of MeOH is about 15.5. Thus, DMSO acts as a strong proton acceptor and it can abstract the proton from HBT* at a higher rate than the typical proton-transfer time constant of an intermediate-strength photoacid. With the time constant of ESHT of 190 fs (or the rate constant of 5.2×10^{12} s^{-1}) from HBT* to DMSO, the barrier is probably very low. Although the exact nature of the high photoacidity of HBT in DMSO is not very clear, and does not correlate well with ΔpK_a of other photoacids, one possible explanation is that the DMSO molecule forms solvated structures of the donor−acceptor complex via strong H-bonding interaction with HBT. Thus, the ESPT rate is mainly limited by an intermolecular vibration between the H donor and acceptor group bridging the HBT−DMSO complex.[43] Additionally, it is worth pointing out that HBT has very different structure, charge delocalization, basicity, and ground-state complex formation compared with other photoacids.

Singlet-to-Triplet Transition. As stated above, the deactivation of the singlet excited state in HBT thus occurs through fluorescence, nonradiative IC, and singlet-to-triplet mechanisms (see Figure 8). In addition, the different relaxation dynamics of excited HBT suggest that the potential energy surface is influenced by the solvent-dependent intramolecular charge redistribution and the hydrogen-bonding geometry in both ground and excited states. Being in this regime, several reports on photophysical behavior of HBT have also suggested that the photoinduced torsional rotation leads to the existence of cis, twisted, and trans keto forms of HBT in the excited state.[29,47] As we observed for excited HBT in different solvents, the existence of the triplet state and twisted HBT proceed from the singlet excited state. In the current study, we demonstrated that the singlet-to-triplet transition depends on the polarity and hydrogen bond capability of the solvent, where the ISC of HBT is more efficient in a solvent with a higher polarity and capability of forming hydrogen bonds. Irrespective of the solvent polarity and the H-bond capability, the ISC occurs exclusively in the keto tautomer because the triplet state is populated after the rapid enol−keto tautomerization. Because the energy of the lowest triplet state of the enol form is higher than that of the keto form,[47] it may be speculated that the triplet state is in the keto form. In particular, the photoexcitation dynamics of HBT are similar to HBO,[19] where both molecules are in the enol form in the ground state and undergo H-transfer via an adiabatic enol−keto tautomer in the first excited singlet state, followed by rotational motion, and then relaxation through a branched pathway via ISC, radiative decay, and nonradiative decay to the keto ground state. In comparison, the photophysical behavior of HBQ, which has rigid molecular conformations, is limited to the ESIHT in both aprotic and protic solvents, the rapid ISC to the triplet state, and other fast nonradiative pathways without any intermolecular H-bonding effects.[20]

4. CONCLUSIONS

We have studied hydrogen transfer in the first excited singlet state of HBT using femtosecond pump−probe spectroscopy in

dx.doi.org/10.1021/jp508777h | J. Phys. Chem. B XXXX, XXX, XXX−XXX

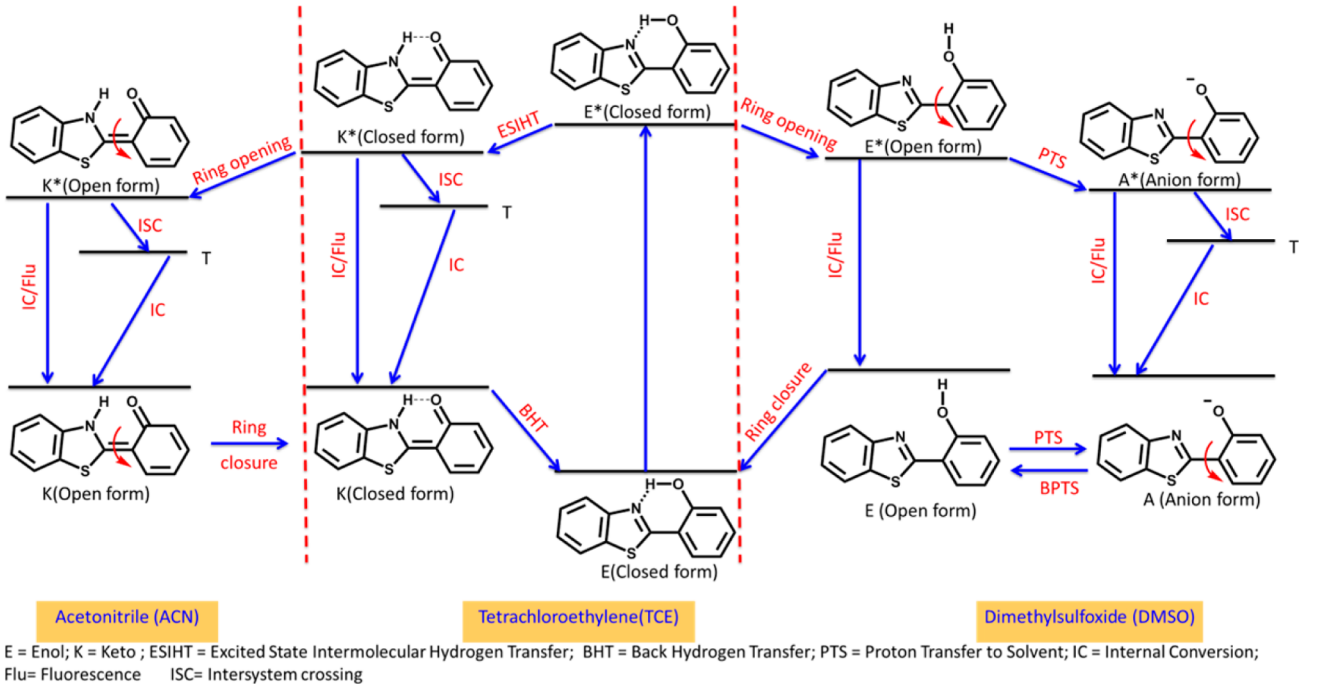


Figure 8. Schematic representation of photophysical changes of HBT in different solvents after excitation.

solvents with different polarities and hydrogen bonding capabilities, and have found that the mechanism for electronic excited-state relaxation is controlled by the solvent polarity. More specifically, in nonpolar solvents, the ground-state HBT molecules adopt a closed form stabilized by O−H···N chelated hydrogen bonds (zero twisting angle around the central C−C bond connecting the hydroxyphenyl and benzothiazole moieties), and only the keto-form emission is observed. In polar solvents, such as ACN and MeOH, such an intramolecular hydrogen bond is strongly disturbed, and emissions from both the enol and keto forms are recorded. The ratio between the enol and keto is very sensitive to the solvent polarity and hydrogen bond capability, as indicated in the steady-state fluorescence data. Immediately after optical excitation, large electronic charge redistribution increases the acidity and the basicity of the donor−acceptor units, leading to ultrafast H transfer from the hydroxyl group to the nitrogen atom, suggesting a barrierless potential energy surface for the excited-state reaction. In contrast, in DMSO, our results indicate that the enol tautomer undergoes intermolecular proton transfer to the solvent, leading to the formation of the excited state of the anionic form. Furthermore, the time-resolved data clearly show the solvent-dependent branching of the exited-state decay to the ground state and the triplet state. To conclude, the relaxation dynamics of excited HBT can be controlled by the solvent-dependent intramolecular charge redistribution and the hydrogen-bonding geometry in the excited state. Finally, the reaction scheme of singlet excited HBT reported here may be valid not only for a wide variety of solvents but also for other intramolecular hydrogen transfer systems.

■ ASSOCIATED CONTENT

Supporting Information

Figure showing TA spectra of HBT dissolved in TCE time delays of 1.01 and 50.7 ps after 350 nm photoexcitation, rescaled to show the change in the signal associated with the vibrational cooling. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: omar.abdelsaboor@kaust.edu.sa.

Notes

The authors declare no competing financial interest.

†S.M.A.: On leave from Chemistry Department, Assiut University, Egypt.

■ ACKNOWLEDGMENTS

S.M.A. is grateful for the postdoctoral fellowship provided by Saudi Basic Industries Corporation (SABIC). The work reported here was supported by the King Abdullah University of Science and Technology.

■ REFERENCES

(1) Formosinho, S. J.; Arnaut, L. G. Excited-State Proton Transfer Reactions II. Intramolecular Reactions. *J. Photochem. Photobiol., A* **1993**, *75*, 21−48.

(2) Douhal, A.; Lahmani, F.; Zewail, A. H. Proton-Transfer Reaction Dynamics. *Chem. Phys.* **1996**, *207*, 477−498.

(3) Zhong, D.; Douhal, A.; Zewail, A. H. Femtosecond Studies of Protein−Ligand Hydrophobic Binding and Dynamics: Human Serum Albumin. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 14056−14061.

(4) Rini, M.; Dreyer, J.; Nibbering, E. T. J.; Elsaesser, T. Ultrafast Vibrational Relaxation Processes Induced by Intramolecular Excited State Hydrogen Transfer. *Chem. Phys. Lett.* **2003**, *374*, 13−19.

(5) Rini, M.; Kummrow, A.; Dreyer, J.; Nibbering, E. T. J.; Elsaesser, T. Femtosecond Mid-Infrared Spectroscopy of Condensed Phase Hydrogen-Bonded Systems as a Probe of Structural Dynamics. *Faraday Discuss.* **2003**, *122*, 27−40.

(6) Nibbering, E. T. J.; Fidder, H.; Pines, E. Ultrafast Chemistry: Using Time-Resolved Vibrational Spectroscopy for Interrogation of Structural Dynamics. *Annu. Rev. Phys. Chem.* **2005**, *56*, 337−367.

(7) Park, S.; Kwon, O.-H.; Lee, Y.-S.; Jang, D.-J.; Park, S. Y. Imidazole-Based Excited-State Intramolecular Proton-Transfer

(ESIPT) Materials: Observation of Thermally Activated Delayed Fluorescence (TDF). *J. Phys. Chem. A* **2007**, *111*, 9649−9653.
(8) Hsieh, C.-C.; Jiang, C.-M.; Chou, P.-T. Recent Experimental Advances on Excited-State Intramolecular Proton Coupled Electron Transfer Reaction. *Acc. Chem. Res.* **2010**, *43*, 1364−1374.
(9) Mohammed, O. F.; Luber, S.; Batista, V. S.; Nibbering, E. T. J. Ultrafast Branching of Reaction Pathways in 2-(2′-Hydroxyphenyl)-benzothiazole in Polar Acetonitrile Solution. *J. Phys. Chem. A* **2011**, *115*, 7550−7558.
(10) Luber, S.; Adamczyk, K.; Nibbering, E. T. J.; Batista, V. S. Photoinduced Proton Coupled Electron Transfer in 2-(2′-Hydroxyphenyl)-Benzothiazole. *J. Phys. Chem. A* **2013**, *117*, 5269−5279.
(11) Mohammed, O. F.; Adamczyk, K.; Banerji, N.; Dreyer, J.; Lang, B.; Nibbering, E. T. J.; Vauthey, E. Direct Femtosecond Observation of Tight and Loose Ion Pairs upon Photoinduced Bimolecular Electron Transfer. *Angew. Chem.* **2008**, *120*, 9184−9188.
(12) Mohammed, O. F.; Kwon, O.-H.; Othon, C. M.; Zewail, A. H. Charge Transfer Assisted by Collective Hydrogen-Bonding Dynamics. *Angew. Chem., Int. Ed.* **2009**, *48*, 6251−6256.
(13) Mohammed, O. F. Ultrafast Intramolecular Charge Transfer of Formyl Perylene Observed Using Femtosecond Transient Absorption Spectroscopy. *J. Phys. Chem. A* **2010**, *114*, 11576−11582.
(14) Wu, J.; Liu, W.; Ge, J.; Zhang, H.; Wang, P. New Sensing Mechanisms for Design of Fluorescent Chemosensors Emerging in Recent Years. *Chem. Soc. Rev.* **2011**, *40*, 3483−3495.
(15) Mohammed, O. F.; Xiao, D.; Batista, V. S.; Nibbering, E. T. J. Excited-State Intramolecular Hydrogen Transfer (ESIHT) of 1,8-Dihydroxy-9,10-anthraquinone (DHAQ) Characterized by Ultrafast Electronic and Vibrational Spectroscopy and Computational Modeling. *J. Phys. Chem. A* **2014**, *118*, 3090−3099.
(16) Elsaesser, T.; Schmetzer, B.; Lipp, M.; Bäuerle, R. J. Excited-State Proton Transfer in 2-(2′-Hydroxyphenyl)benzothiazole: Transient Electronic Absorption Measured on the Picosecond Time Scale. *Chem. Phys. Lett.* **1988**, *148*, 112−118.
(17) Laermer, F.; Elsaesser, T.; Kaiser, W. Femtosecond Spectroscopy of Excited-State Proton Transfer in 2-(2′-Hydroxyphenyl)-benzothiazole. *Chem. Phys. Lett.* **1988**, *148*, 119−124.
(18) Frey, W.; Laermer, F.; Elsaesser, T. Femtosecond Studies of Excited-State Proton and Deuterium Transfer in Benzothiazole Compounds. *J. Phys. Chem.* **1991**, *95*, 10391−10395.
(19) Mordzinski, A.; Grellmann, K. H. Excited-State Proton-Transfer Reactions in 2-(2′-hydroxyphenyl)benzoxazole. Role of Triplet States. *J. Phys. Chem.* **1986**, *90*, 5503−5506.
(20) Chou, P.-T.; Wei, C.-Y. Photophysics of 10-Hydroxybenzo[h]-quinoline in Aqueous Solution. *J. Phys. Chem.* **1996**, *100*, 17059−17066.
(21) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K. Investigation of the Dynamic Processes of the Excited States of o-Hydroxybenzaldehyde and o-Hydroxyacetophenone by Emission and Picosecond Spectroscopy. *J. Am. Chem. Soc.* **1983**, *105*, 4220−4226.
(22) Stock, K.; Bizjak, T.; Lochbrunner, S. Proton Transfer and Internal Conversion of o-Hydroxybenzaldehyde: Coherent versus Statistical Excited-State Dynamics. *Chem. Phys. Lett.* **2002**, *354*, 409−416.
(23) Lochbrunner, S.; Wurzer, A. J.; Riedle, E. Microscopic Mechanism of Ultrafast Excited-State Intramolecular Proton Transfer: A 30-fs Study of 2-(2′-Hydroxyphenyl)-benzothiazole. *J. Phys. Chem. A* **2003**, *107*, 10580−10590.
(24) Takeuchi, S.; Tahara, T. Coherent Nuclear Wavepacket Motions in Ultrafast Excited-State Intramolecular Proton Transfer: Sub-30-fs Resolved Pump-Probe Absorption Spectroscopy of 10-Hydroxybenzo-[h]quinoline in Solution. *J. Phys. Chem. A* **2005**, *109*, 10199−10207.
(25) Schriever, C.; Barbatti, M.; Stock, K.; Aquino, A. J. A.; Tunega, D.; Lochbrunner, S.; Riedle, E.; de Vivie-Riedle, R.; Lischka, H. The Interplay of Skeletal Deformations and Ultrafast Excited-State Intramolecular Proton Transfer: Experimental and Theoretical Investigation of 10-Hydroxybenzo[h]quinoline. *Chem. Phys.* **2008**, *347*, 446−461.
(26) Stock, K.; Schriever, C.; Lochbrunner, S.; Riedle, E. Reaction Path Dependent Coherent Wavepacket Dynamics in Excited State Intramolecular Double Proton Transfer. *Chem. Phys.* **2008**, *349*, 197−203.
(27) Elsaesser, T.; Kaiser, W. Visible and Infrared Spectroscopy of Intramolecular Proton Transfer using Picosecond Laser Pulses. *Chem. Phys. Lett.* **1986**, *128*, 231−237.
(28) Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. Intramolecular Proton Transfer and Excited-State Relaxation in 2-(2-Hydroxyphenyl)-benzothiazole. *J. Am. Chem. Soc.* **1980**, *102*, 5631−5635.
(29) Al-Soufi, W.; Grellmaan, K. H.; Nickel, B. Triplet State Formation and cis-trans Isomerization in the Excited Singlet State of the keto Tautomer of 2-(2′-Hydroxyphenyl)benzothiazole. *Chem. Phys. Lett.* **1990**, *174*, 609−616.
(30) Potter, C. A. S.; Brown, R. G.; Vollmer, F.; Rettig, W. Role of Twisted Intramolecular Charge-transfer States in the Decay of 2-(2′-Hydroxyphenyl)benzothiazole following Excited-state Intramolecular Proton Transfer. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 59−67.
(31) Nosenko, Y.; Wiosna-Sałyga, G.; Kunitski, M.; Petkova, I.; Singh, A.; Buma, W. J.; Thummel, R. P.; Brutschy, B.; Waluk, J. Proton Transfer with a Twist? Femtosecond Dynamics of 7-(2-Pyridyl)-indole in Condensed Phase and in Supersonic Jets. *Angew. Chem.* **2008**, *120*, 6126−6129.
(32) Barbatti, M.; Aquino, A. J. A.; Lischka, H.; Schriever, C.; Lochbrunner, S.; Riedle, E. Ultrafast Internal Conversion Pathway and Mechanism in 2-(2′-Hydroxyphenyl)benzothiazole: A Case Study for Eexcited-State Intramolecular Proton Transfer Systems. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1406−1415.
(33) de Vivie-Riedle, R.; Waele, V. D.; Kurtz, L.; Riedle, E. Ultrafast Excited-State Proton Transfer of 2-(2′-Hydroxyphenyl)benzothiazole: Theoretical Analysis of the Skeletal Deformations and the Active Vibrational Modes. *J. Phys. Chem. A* **2003**, *107*, 10591−10599.
(34) Wang, R.; Liu, D.; Xu, K.; Li, J. Substituent and Solvent Effects on Excited State Intramolecular Proton Transfer in Novel 2-(2′-Hydroxyphenyl)benzothiazole Derivatives. *J. Photochem. Photobiol., A* **2009**, *205*, 61−69.
(35) El-Ballouli, A. O.; Alarousu, E.; Usman, A.; Pan, J.; Bakr, O. M. Mohammed, O. F. Real-Time Observation of Ultrafast Intraband Relaxation and Exciton Multiplication in PbS Quantum Dots. *ACS Photonics* **2014**, *1*, 285−292.
(36) Aly, S. M.; Parida, M. R.; Alarousu, E.; Mohammed, O. F. Ultrafast Electron Injection at the Cationic Porphyrin-Graphene Interface Assisted by Molecular Flattening. *Chem. Commun.* **2014**, *50*, 10452−10455.
(37) Chou, P.-T.; Yu, W.-S.; Cheng, Y.-M.; Pu, S.-C.; Yu, Y.-C.; Lin, Y.-C.; Huang, C.-H.; Chen, C.-T. Solvent-Polarity Tuning Excited-State Charge Coupled Proton-Transfer Reaction in p-N,N-Ditolylaminosalicylaldehydes. *J. Phys. Chem. A* **2004**, *108*, 6487−6498.
(38) Holm, A.-K.; Mohammed, O. F.; Rini, M.; Mukhtar, E.; Nibbering, E. T. J.; Fidder, H. Sequential Merocyanine Product Isomerization Following Femtosecond UV Excitation of a Spiropyran. *J. Phys. Chem. A* **2005**, *109*, 8962−8968.
(39) Fujino, T.; Arzhantsev, S. Y.; Tahara, T. Femtosecond Time-Resolved Fluorescence Study of Photoisomerization of trans-Azobenzene. *J. Phys. Chem. A* **2001**, *105*, 8123−8129.
(40) Chang, C.-W.; Lu, Y.-C.; Wang, T.-T.; Diau, E. W.-G. Photoisomerization Dynamics of Azobenzene in Solution with S1 Excitation: A Femtosecond Fluorescence Anisotropy Study. *J. Am. Chem. Soc.* **2004**, *126*, 10109−10118.
(41) Ishii, K.; Takeuchi, S.; Tahara, T. A 40-fs Time-Resolved Absorption Study of Cis-Stilbene in Solution: Observation of Coherent Nuclear Wavepacket Motion in Reactive Excited State. *Ultrafast Phenomena XIV Springer Series in Chemical Physics* **2005**, *79*, 459−461.
(42) Koller, F. O.; Schreier, W. J.; Schrader, T. E.; Sieg, A.; Malkmus, S.; Schulz, C.; Dietrich, S.; Ruck-Braun, K.; Zinth, W.; Braun, M. Ultrafast Structural Dynamics of Photochromic Indolylfulgimides Studied by Vibrational Spectroscopy and DFT Calculations. *J. Phys. Chem. A* **2006**, *110*, 12769−12776.

(43) Simkovitch, R.; Shomer, S.; Gepshtein, R.; Huppert, D. How Fast Can a Proton-Transfer Reaction be Beyond the Solvent-Control Limit? *J. Phys. Chem. B* **2014**, DOI: 10.1021/jp506011e.
(44) Roberts, E. L.; Dey, J.; Warner, I. M. Ground- and Excited-State Structural Orientation of 2-(2′-Hydroxyphenyl)benzazoles in Cyclodextrins. *J. Phys. Chem.* **1996**, *100*, 19681−19686.
(45) Potter, C. A. S.; Brown, R. G. Excites-State Intramolecular Proton Transfer in Polar Solutions of 2-(2′-Hydroxyphenyl)-benzothiazole. *Chem. Phys. Lett.* **1988**, *153*, 7−12.
(46) Durmis, J.; Karvaš, M.; Maňásek, Z. 2-Aryl Derivatives of Condensed Five-Membered N-Heterocyclic Compounds. I. Dissociation Constants of 2- and 4-Substituted Phenols and Naphthols. *Collect. Czech. Chem. Commun.* **1973**, *38*, 215−223.
(47) Chou, P.-T.; Studer, S. L.; Martinez, M. L. Studies of the triplet state of 2-(2′-hydroxyphenyl)benzothiazole. *Chem. Phys. Lett.* **1991**, *178*, 393−398.