

# Excited-State Proton-Transfer Dynamics of 7-Hydroxyquinoline in Room Temperature Ionic Liquids

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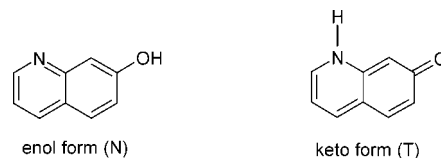
Excited-state proton transfer (ESPT) reaction of 7-hydroxyquinoline (7-HQ) mediated by methanol molecules has been studied in two room temperature ionic liquids (RTILs) using steady-state and time-resolved fluorescence measurements. While no ESPT is observable in neat RTILs, characteristic tautomer fluorescence of 7-HQ could be observed in the presence of small quantity of methanol (0.5–4.1 M). The observation of a rise time (350 ps–1.4 ns) associated with the tautomer fluorescence suggests that proton transfer in 7-HQ is indeed an excited-state phenomenon that requires considerable solvent reorganization prior to the relay of proton from the hydroxyl group to the distant ring nitrogen atom through suitably organized dimeric chain of methanol molecules. The rise time of the tautomer fluorescence, which has been found to decrease with increasing methanol concentration, is attributed to the change of viscosity of the medium upon methanol addition. While the influence of viscosity on the ESPT kinetics is evident from the data, lack of any definite correlation between the bulk viscosity and the rise time has been interpreted in terms of the microheterogeneous nature of the media that does not allow assessment of the microviscosity around 7-HQ from the bulk viscosity.

## 1. Introduction

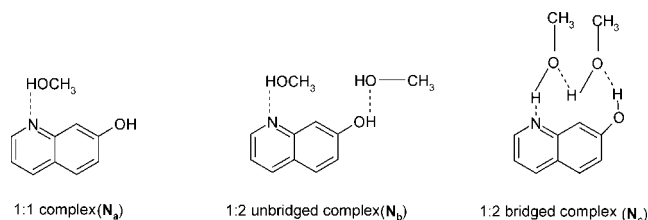
Room temperature ionic liquids (RTILs) are salts comprising most often an organic cation and an inorganic anion with melting point below the room temperature. These substances continue to receive great attention from the researchers worldwide<sup>1–4</sup> primarily because of the potential of these substances as green alternatives to the volatile organic solvents. We have been studying various photoinduced processes in these media primarily to obtain an understanding of the structure, dynamics, and properties of the RTILs.<sup>5–10</sup> Our studies have also been directed toward finding out how the viscosity, polarity, and charged constituents of these media can influence the photo-physical behavior of some photosystems of interest.<sup>5–10</sup> These studies and several others in recent years have indicated a complex nature of these media. In particular, static and dynamic heterogeneity of these media is one of the talking points of the RTILs.<sup>5,7,9,11,12</sup>

Since proton transfer reactions play a central role in a wide variety of chemical and biological phenomena<sup>13</sup> and that there is hardly any study of the proton transfer reaction involving photoexcited molecules in RTILs, we have undertaken this work on 7-hydroxyquinoline (7-HQ, Chart 1), an amphoteric molecule that contains both acidic (–OH group) and basic (–N = group) moieties. Unlike a commonly encountered excited-state intramolecular proton transfer (ESIPT) reaction such as in 3-hydroxyflavone (3-HF),<sup>14</sup> where the proton moves from the hydroxy group to an adjacent carbonyl group on photoexcitation without the involvement of the solvent molecules, the excited-state proton transfer (ESPT) reaction in 7-HQ requires participation of protic solvent molecules, as the functional groups involved are far apart.<sup>15–21</sup> Since this process closely resembles proton relay over large distance observed in several systems, 7-HQ serves as a simple model system for understanding the

## CHART 1: Enol and Keto Forms of 7-Hydroxyquinoline



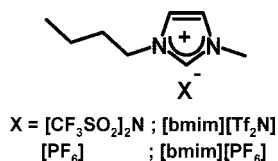
## CHART 2: Various Hydrogen-Bonded Enol Forms of 7-Hydroxyquinoline with Methanol



mechanism of long distance proton translocation mediated by a hydrogen bonded network.

Extensive fluorescence studies have indicated that ESPT reaction in 7-HQ proceeds through the formation of 1:2 complexes (7HQ/(ROH)<sub>2</sub>; Chart 2) in monohydroxy alcohols such as in methanol or in hexane-alcohol.<sup>15–22</sup> However, in polyhydroxy alcohols such as glycerol (GL) or ethylene glycol (EG), a single alcohol molecule can give rise to ESPT in the system through 1:1 complexation.<sup>23</sup> The rate constant of ESPT in the complex is found to be dependent on the H-bond donating ability of the alcohols, as measured by the Kamlet–Taft acidity ( $\alpha$ ) of the alcohols.<sup>21,24</sup> In a recent work, Jang and co-workers<sup>21</sup> have demonstrated that ESPT in 7HQ/(ROH)<sub>2</sub> complexes in *n*-alkanes is characterized by an unusually large temperature independent and viscosity dependent kinetic isotope effect. It is shown that ESPT in this system is initiated by proton transfer from alcohol molecule to the imino nitrogen atom of 7-HQ and is completed by rapid proton transfer from the enol group of

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**CHART 3: Structures and Abbreviations of the Ionic Liquids Used in the Present Work<sup>a</sup>**

<sup>a</sup> [bmim] = 1-butyl-3-methylimidazolium, [Tf<sub>2</sub>N] = bis(trifluoromethanesulfonyl)imide.

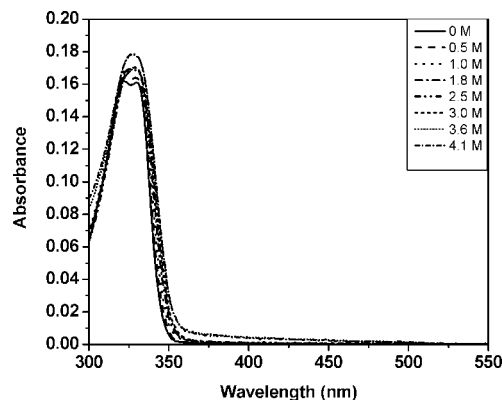
the molecule to the transient alkoxide moiety. Interestingly, in viscous media such as in GL and EG<sup>23</sup> as well as in argon<sup>25</sup> and polymer matrices,<sup>26</sup> the keto-tautomer of 7-HQ has been observed in the ground state but not in conventional less viscous media like hexane-alcohol, alcohols, and so forth.

While ESPT reaction such as in 3-HF is hardly dependent on the viscosity of the media because of its intrinsic nature, Douhal and co-workers<sup>23</sup> have shown that solvent viscosity plays an important role in determining the dynamics of solvent mediated proton transfer reaction in 7-HQ. This has later been confirmed by Jang and co-workers.<sup>21</sup> Since two monohydroxy alcohol molecules are required to bridge the proton donor and acceptor sites of 7-HQ for ESPT in the system and viscosity of the medium plays a crucial role in it, we realized that this system provides an opportunity to investigate the influence of viscous RTILs on the mechanism and kinetics of the ESPT process. A number of specific issues that we have addressed apart from the influence of viscosity are the following. First, since the C-2 hydrogen of the imidazolium cation is acidic and known to be hydrogen bonded to the H-bond acceptors such as the anionic component of the RTILs, it is of interest to find out whether the hydrogen bonded network available in the RTILs can reorganize to give rise to ESPT in 7-HQ. Second, it is also of interest to find out whether a small amount of methanol can break the hydrogen bonded network of the viscous RTILs and form a bridge consisting of two methanol molecules that is essential for ESPT in 7-HQ. Third, unlike the conventional solvents, where the constituents are neutral molecules, RTIL provides an opportunity to study how/whether its ionic constituents can influence the long distance movements of proton in 7-HQ. In this work, methanol mediated ESPT reaction of 7-HQ has been studied in two RTILs, [bmim][Tf<sub>2</sub>N] and [bmim][PF<sub>6</sub>] (Chart 3), which differ in their viscosities significantly.

**2. Materials and Methods**

The ILs were synthesized according to the published procedure.<sup>2,27</sup> The purification procedures adopted for the ILs have been described elsewhere.<sup>28</sup> All ILs were kept under vacuum before experiment. 7-HQ was procured from Acros and further recrystallized from ethanol prior to use. Dry methanol was obtained on refluxing methanol with magnesium turnings and iodine. The magnesium methoxide formed reacts with any water present to form the highly insoluble magnesium hydroxide. The methanol was then slowly distilled off.

The absorption and steady-state fluorescence spectra were recorded on a UV-visible spectrophotometer (Cary100, Varian) and a spectrofluorimeter (FluoroLog-3, Jobin Yvon), respectively. The fluorescence spectra were corrected for the instrumental response. Time-resolved fluorescence measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrometer (5000, IBH). NanoLED ( $\lambda_{\text{exc}} = 331 \text{ nm}$ ) was used as the excitation source, and an MCP photomultiplier



**Figure 1.** Absorption spectra of 7-HQ in [bmim][Tf<sub>2</sub>N] for different concentrations of methanol (0–4.1 M). Any absorption due to the RTILs in this region has been eliminated by baseline correction with neat [bmim][Tf<sub>2</sub>N].

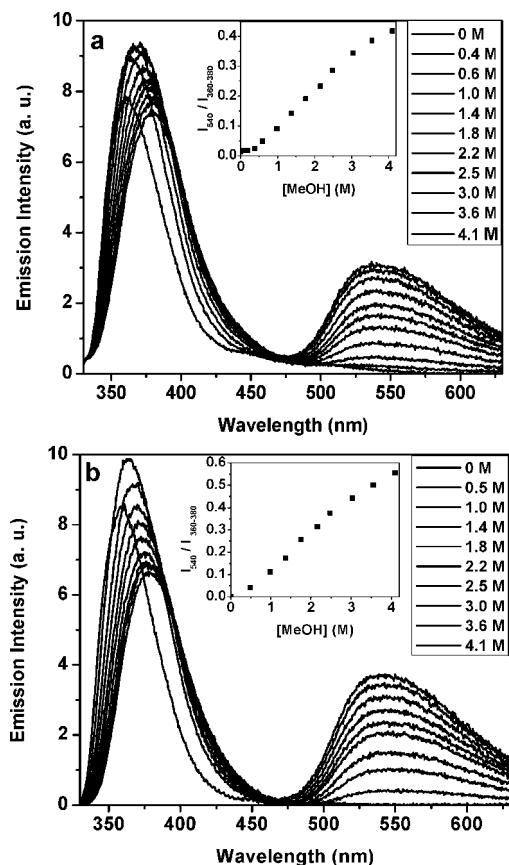
(Hamamatsu R3809U-50) was used as the detector with a response time of 40 ps. The width of the instrument function, which was limited by the fwhm of the excitation source, was 1 ns. The lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (version 2.2) decay analysis software. The quality of the fits was measured by the  $\chi^2$  values and distribution of residuals.

**3. Results**

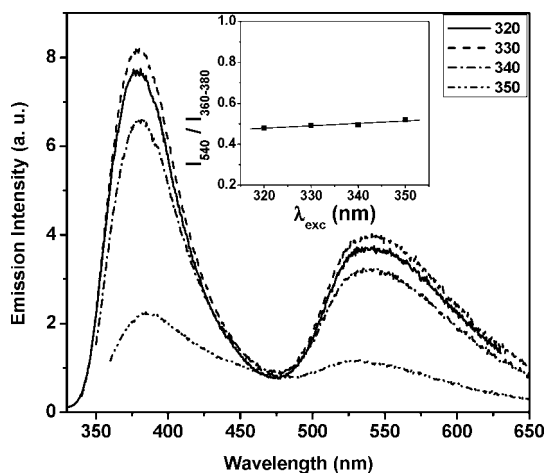
**3.1. Steady State Behavior.** The absorption spectra of 7-HQ in RTILs are found similar to that observed in acetonitrile.<sup>23</sup> With gradual addition of methanol, the vibrational structure of the main absorption band is lost and enhanced absorption in the long wavelength region can be observed (Figure 1). These changes are similar to those observed in acetonitrile–glycerol or acetonitrile–ethylene glycol systems.<sup>23</sup> A similar enhancement of absorption is also observed in hexane–methanol.<sup>20,22</sup>

7-HQ in neat RTILs, when excited at around 320–330 nm, shows a single emission band with maximum at 360 nm (Figure 2), a behavior very similar to that observed in acetonitrile.<sup>23</sup> On addition of methanol, dual emission with maxima at 360–380 and 540 nm (Figure 2) is observed. The changes observed around the 360 nm band (small shift and changes in intensity) in the presence of methanol are similar to those observed for the system in hexane–methanol or in acetonitrile–glycerol/ethylene glycol. With an increase in concentration of methanol, a small decrease in intensity of the short wavelength emission band is accompanied with a noticeable increase in the intensity of the green emission at 540 nm. The variation of the ratio of the fluorescence intensities at 540 nm and 360–380 nm is shown in Figure 2.

A study of the excitation wavelength dependence of the fluorescence behavior reveals the following: With increase in the excitation wavelength, the overall fluorescence intensity of the system is decreased progressively (Figure 3). However, no significant change in the relative intensities of the two emission bands is observed. This is evident from the insert to Figure 3. The dual emission of 7-HQ could be observed up to an excitation wavelength of 350 nm. For excitation wavelengths higher than 350 nm, where the absorption due to 7-HQ is very low, the emission due to the imidazolium ionic liquids starts interfering with the measurements.<sup>28</sup> However, it is found that the 540 nm emission band due to 7-HQ could not be observed for excitation wavelength higher than 375 nm. The steady state



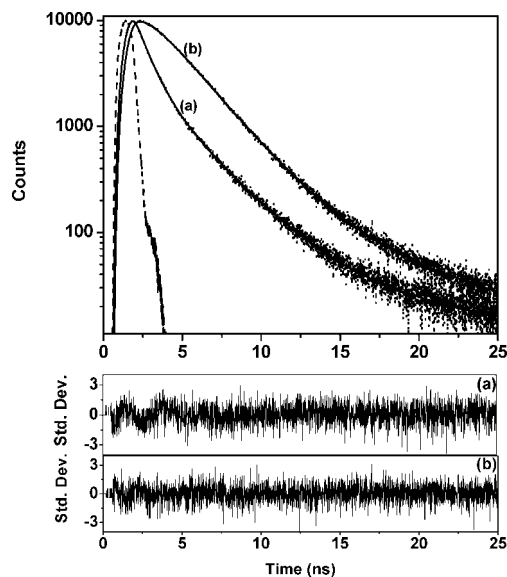
**Figure 2.** Fluorescence spectra of 7-HQ in [bmim][Tf<sub>2</sub>N] (a) and [bmim][PF<sub>6</sub>] (b) for different concentrations of methanol (0–4.1 M).  $\lambda_{\text{exc}} = 320$  nm. Weak emission due to neat RTILs was subtracted from each of the spectra. The individual emission spectra of 7-HQ and RTILs (before subtraction) are provided as Supporting Information. Inset shows variation of  $I_{540}/I_{360-380}$  with concentration of methanol.  $I_{360-380}$  was measured at the wavelength where the fluorescence intensity is maximum.



**Figure 3.** Emission spectra of 7-HQ in [bmim][PF<sub>6</sub>] with 3.6 M methanol for different excitation wavelengths. Inset shows  $I_{540}/I_{360-380}$  variance with excitation wavelength.

fluorescence behavior of 7-HQ in two RTILs in the presence of methanol is found qualitatively rather similar.

**3.2. Time-Resolved Behavior.** In order to obtain information on the dynamics of the ESPT process, the fluorescence decay behavior of the system has been studied monitoring the short wavelength (360–380 nm region) and long wavelength (540 nm) emission bands. Representative decay profiles are shown



**Figure 4.** Fluorescence decay profiles of 7-HQ in [bmim][Tf<sub>2</sub>N] at 360 (a) and 540 nm (b) for MeOH concentration of 1.8 M. The experimental decay profiles are indicated by the dots and the instrument profile as dashes. The solid lines represent the best-fit to the decay curves. The residuals are indicated below for the respective decay profiles.

in Figure 4. The various decay parameters corresponding to the two emission bands for different concentrations of methanol in two RTILs are collected in Table 1 and Table 2. The decay profiles are found to be biexponential for both bands. However, while at the 360–380 nm region, both of the components decay with time, the time profile of the 540 nm band is characterized by a negative pre-exponential factor (i.e., a rise component). It can be seen that the lifetime components associated with the two monitoring wavelengths are not identical. The rise component at 540 nm however is similar to one of the decay components of the short wavelength band. The lifetime values associated with the rise time and the corresponding time constant at 360 nm generally decrease with an increase in the concentration of methanol. This is evident from the fact that, in [bmim][Tf<sub>2</sub>N], the short component at 360 nm decreases from 1.25 ns to 450 ps, while the long component decreases only slightly from 3.8 to 2.9 ns. At 540 nm, the rise time decreases from 1.35 ns to 370 ps, whereas the long component remains constant at around 2.7 ns. In [bmim][PF<sub>6</sub>], similar changes are apparent from the data shown in Table 2. At 360–380 nm, the short decay time varies from 1.01 ns to 580 ps, while the longer one remains more or less constant around 2.5 ns. The rise time observed at 540 nm decreases from 1.22 ns to 350 ps with an increase in concentration of methanol while the second decay time remains constant at ~2.5 ns (Table 2).

#### 4. Discussion:

**4.1. Steady State Spectral Studies.** The structured absorption band of 7-HQ in neat RTILs suggests that the molecule experiences an environment similar to that in polar aprotic solvent such as in acetonitrile.<sup>23</sup> The enhanced absorption in the longer wavelength region in presence of methanol is consistent with the literature, and is commonly attributed to the formation of H-bonded complexes of 7-HQ with methanol.<sup>20,22</sup> The absence of any isosbestic point in the absorption spectra in the presence of methanol indicates that 7-HQ and methanol form complexes of different stoichiometries. This conclusion is in agreement with the literature, which clearly suggests that 7-HQ forms 1:1 and 1:2 (bridged and unbridged) complexes

**TABLE 1: Time Resolved Fluorescence Data<sup>a</sup> of 7-HQ in [bmim][Tf<sub>2</sub>N],  $\lambda_{\text{exc}} = 331$  nm**

[MeOH] (M)	decay parameters at				$\chi^2_{360,540}$
	360 nm		540 nm		
	$\tau_1$ (a <sub>1</sub> )	$\tau_2$ (a <sub>2</sub> )	$\tau_1$ (a <sub>1</sub> )	$\tau_2$ (a <sub>2</sub> )	
0 (49 cP) <sup>b</sup>	1.02 (98.8)	4.91 (1.1)			1.2
0.6	1.25 (94.9)	3.82 (5.0)	1.36 (−31.3)	2.75 (65.6)	1.3, 1.1
1.0	1.23 (92.5)	3.81 (7.5)	1.18 (−36.5)	2.55 (62.3)	1.3, 1.05
1.4	1.12 (88.7)	3.51 (11.2)	1.0 (−37.6)	2.45 (61.5)	1.3, 1.06
1.8	0.79 (79.5)	2.69 (20.1)	0.85 (−37.5)	2.39 (61.7)	1.07, 1.05
2.2	0.73 (77.8)	2.76 (21.8)	0.72 (−36.2)	2.43 (63.1)	1.08, 1.06
2.5	0.64 (76.8)	2.82 (22.8)	0.6 (−35.2)	2.49 (64.2)	1.1, 1.07
3.0	0.58 (63.6)	2.92 (36.1)	0.48 (−35.9)	2.53 (63.5)	1.07, 1.07
3.6	0.53 (62.5)	3.0 (37.2)	0.42 (−36.2)	2.73 (63.7)	1.09, 1.3
4.1 (16.6 cP) <sup>b</sup>	0.45 (61.7)	2.88 (38)	0.37 (−44.8)	2.7 (55.1)	1.06, 1.15

<sup>a</sup> The small percentage of the second lifetime component for [methanol] = 0 is probably due to the RTIL. The amplitudes associated with the two lifetime components in the presence of methanol add to 96.9–99.9 indicating the presence of a very small percentage (0.1–3.1%) of another component with a long lifetime component, which is probably due to RTIL. Since fwhm of the excitation source is  $\sim 1$  ns, lifetime values lower than 1 ns merely indicate the trend, and too much importance should not be attached to the absolute values. <sup>b</sup> Viscosity measured<sup>29</sup> for 0 and 4.1 M MeOH at 25 °C.

**TABLE 2: Time Resolved Fluorescence Data<sup>a</sup> of 7-HQ [bmim][PF<sub>6</sub>],  $\lambda_{\text{exc}} = 331$  nm**

[MeOH] (M)	decay parameters at				$\chi^2_{360,540}$
	360 nm		540 nm		
	$\tau_1$ (a <sub>1</sub> )	$\tau_2$ (a <sub>2</sub> )	$\tau_1$ (a <sub>1</sub> )	$\tau_2$ (a <sub>2</sub> )	
0 (260 cP) <sup>b</sup>	0.88 (96.7)	2.45 (3.3)			1.3
0.5	1.01 (86.9)	2.23 (13.1)	1.22 (−31.8)	2.57 (62.5)	1.18, 1.1
0.8	1.03 (87.4)	2.45 (12.6)	1.12 (−39.7)	2.31 (58.5)	1.18, 1.09
1.4	0.93 (83.2)	2.55 (16.8)	0.90 (−40)	2.24 (59.5)	1.2, 1.03
1.8	0.86 (81.6)	2.8 (18.4)	0.75 (−38)	2.3 (62)	1.15, 1.03
2.4	0.77 (66.6)	2.8 (32.5)	0.6 (−36)	2.35 (63.3)	1.21, 1.05
4.1 (94 cP) <sup>b</sup>	0.58 (51.5)	2.83 (48.5)	0.35 (−34.5)	2.51 (62.8)	1.25, 1.03

<sup>a</sup> The small percentage of the second lifetime component for [methanol] = 0 is probably due to the RTIL. The amplitudes associated with the two lifetime components in the presence of methanol add to 94.3–99.5 indicating the presence of a small percentage (0.5–5.7%) of another component with a long lifetime component, which is probably due to RTIL. Since fwhm of the excitation source is  $\sim 1$  ns, lifetime values lower than 1 ns merely indicate the trend, and too much importance should not be attached to the absolute values. <sup>b</sup> Viscosity measured<sup>29</sup> for 0 and 4.1 M MeOH at 25 °C.

with monohydroxy alcohols.<sup>20–22,24</sup> In this context, we note that there are reports<sup>23,25,26</sup> that in viscous condition 1:2 bridged H-bonded complex of 7-HQ often forms the tautomer in the ground state, which also contributes to the absorption in the long wavelength region. The absorption maximum of the tautomer is reported to be around 420–430 nm. However, in RTILs, such tautomer formation in the ground state could not be detected from the UV–vis absorption measurements.

As far as fluorescence behavior is concerned, the emission around 360–380 nm region is attributed to the enolic form of 7-HQ in aprotic media and to the free and various H-bonded enol forms of the molecule in protic media.<sup>16,17,20–22,24</sup> The green emission of 7-HQ, which is observed only in protic media, is attributed to the tautomer.<sup>16,17,20–22,24</sup> Since the 540 nm emission could not be observed in neat RTILs, it can be concluded that the imidazolium cation, which serves as an H-bond donor through the C-2 hydrogen, cannot form a H-bonded network with 7-HQ that allows ESPT in the system in the absence of methanol.

As stated previously, extensive studies have indicated that free enol and various H-bonded forms of 7-HQ emit around 360–380 nm region and that these species could not be distinguished by their emission spectra. Hence, the changes observed around this region in the presence of methanol are to be attributed to the formation of the species, which include free enol and its 1:1, 1:2 bridged and 1:2 unbridged complexes. While the blue emission at 360–380 is assigned to the various

uncomplexed and complexed enol forms of 7-HQ, the green fluorescence is attributed to the tautomer.<sup>19</sup> The observation of the 540 nm emission in the presence of methanol indicates that ESPT of 7-HQ does occur in RTILs when methanol is present. This implies that methanol molecules can break the existing network of the RTILs and also form the bridged configuration, which eventually gives rise to the formation of the tautomer.

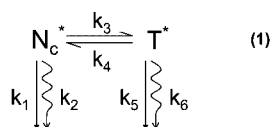
The excitation wavelength dependent emission studies confirm lack of formation of the 7-HQ tautomer in the ground state in RTILs. This may not be surprising as the microviscosity around 7-HQ is significantly lower than that necessary for the formation of tautomer even in the presence of small quantity of methanol.

The dependence of the intensity of the 540 nm emission band on methanol concentration may appear surprising as it is reported that methanol concentration does not affect the dynamics of the ESPT reaction in this system. However, it is shown in the following section that dependence of the tautomer emission intensity in RTILs is the result of a large change in viscosity of the medium and consequent change in the ESPT kinetics on methanol addition.

**4.2. Time-Resolved Spectral Studies.** Fluorescence decays monitored at different emission wavelengths give a clear picture of the excited-state dynamics. If the mechanism of ESPT in RTILs is governed by eq 1, which involves an equilibrium between  $\text{N}_\text{C}^*$  and  $\text{T}^*$  in the excited state, the time profiles of



the two species are then given by eqs 2 and 3 implying that the two decay times associated with  $N_c^*$  and  $T^*$  are identical.



$$[N_c^*] = \frac{[N_c^*]_0}{\lambda_2 - \lambda_1} [(\lambda_2 - X)e^{-\lambda_1 t} + (X - \lambda_1)e^{-\lambda_2 t}] \quad (2)$$

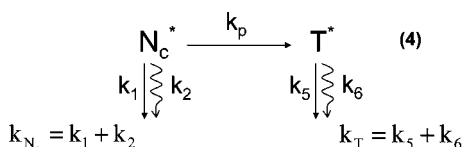
$$[T^*] = \frac{k_3[N_c^*]_0}{\lambda_2 - \lambda_1} [e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (3)$$

where,  $X = k_1 + k_2 + k_3$ ,  $Y = k_4 + k_5 + k_6$

$$\lambda_1 = \frac{1}{2} \left\{ (X + Y) - [(X - Y)^2 + 4k_3k_4]^{1/2} \right\}$$

$$\lambda_2 = \frac{1}{2} \left\{ (X + Y) + [(X - Y)^2 + 4k_3k_4]^{1/2} \right\}$$

However, if the equilibrium between the two species is not established in the excited-state and the formation of  $T^*$  from  $N_c^*$  is represented by eq 4, the time dependence of  $N_c^*$  and  $T^*$  are given by eqs 5 and 6, according to which  $N_c^*$  should show a single exponential decay and  $T^*$  exhibit a rise time identical with the decay time of  $N_c^*$  and a decay time that represents the lifetime of  $T^*$  under the experimental condition.



$$[N_c^*] = [N_c^*]_0 e^{-(k_{N_c} + k_p)t} \quad (5)$$

$$[T^*] = \left( \frac{[N_c^*]_0 k_p}{k_{N_c} + k_p - k_T} \right) [e^{-k_T t} - e^{-(k_{N_c} + k_p)t}] \quad (6)$$

It appears that the present kinetic data in RTILs (Tables 1 and 2) are not consistent with either of the mechanisms. However, the data can be easily interpreted in terms of the second mechanism when one also considers the fact that various enol forms ( $N$ ,  $N_a$ ,  $N_b$ , and  $N_c$ ) of 7-HQ contribute to emission around the same wavelength region (360–380 nm),<sup>21,23,30,31</sup> but only one of them, specifically  $N_c^*$ , is responsible for the formation of  $T^*$ . This implies that the second decay time (the long component) associated with the 360–380 nm emission arises from the free and H-bonded enol forms of 7-HQ, which do not contribute to ESPT, that is,  $N$ ,  $N_a$ , and  $N_b$ . In fact, a similar mechanism is used to account for the time-resolved data of 7-HQ in conventional solvents. The short time-constant, which decreases with an increasing amount of methanol, is due to  $N_c^*$  from which the tautomer is produced. This decay time matches reasonably well with the rise time of the tautomer emission at 540 nm. The rise time, which is the reciprocal of the rate constant of the ESPT reaction, decreases with increasing amount of methanol. It should be noted in this context that Jang

and co-workers did not observe any variation of the rise time of the tautomer emission of 7-HQ in alkanes with methanol concentration. However, this result is not surprising when one considers the change in viscosity of the media on addition of methanol in the two cases and its influence on the ESPT kinetics. It is well-known that ESPT in  $N_c^*$  requires readjustment or fluctuation of the solvent nuclear coordinates prior to complete transfer of proton. Therefore, the rate determining step of ESPT in 7-HQ is determined by the rate at which solvent molecules readjust to facilitate ESPT. Since the viscosity of the medium is lowered on addition of methanol (from 260 to 94 cP in [bmim][PF<sub>6</sub>] and from 49 to 16.6 cP in [bmim][Tf<sub>2</sub>N] in the presence of 4.1 M methanol), the solvent reorganization becomes faster and so does the rise time for the ESPT process. However, when the ESPT process is studied in less viscous alkanes, the change of viscosity on addition of methanol is not so appreciable, and hence, the influence of the effect of methanol on the rise time is not evident.

ESPT of 7-HQ in RTILs is expected to be slow because of the viscous nature of the media and the requirement of conformational readjustments prior to the proton transfer process. The influence of high viscosity of the RTILs is evident from the long rise time of the tautomer fluorescence observed for small concentrations of methanol. In the presence of 0.49–0.59 M methanol, the rise times are in the range of 1.2–1.4 ns. These values are considerably higher than those in conventional solvents clearly due to the viscous nature of the RTILs. However, a close look into these values reveals that the viscosity dependence is not so straightforward and the rise times are not solely determined by the bulk viscosities of the media. Even though [bmim][PF<sub>6</sub>] is more than 5 times viscous than [bmim][Tf<sub>2</sub>N], the rise times in [bmim][PF<sub>6</sub>] are slightly lower than those in [bmim][Tf<sub>2</sub>N] for similar quantity of methanol. For example, in the presence of 0.49 M methanol, the rise time in [bmim][PF<sub>6</sub>] is 1.2 ns, whereas in less viscous [bmim][Tf<sub>2</sub>N] in the presence of 0.59 M methanol, the value is higher at 1.4 ns. One can also compare the rise times listed in the last row of the two tables. In the presence of 4.1 M methanol, when the bulk viscosity of [bmim][PF<sub>6</sub>] is 94 cP, the rise time is measured to be 346 ps. On the other hand, under similar condition, the bulk viscosity of [bmim][Tf<sub>2</sub>N] is much lower (16.6 cP) and yet, the rise time is very similar (367 ps). These results can only be explained when the viscosity around 7-HQ is quite different from the measured bulk viscosity of the RTILs. Considering the microheterogeneous nature of the RTILs, which has been indicated in recent studies,<sup>5,7,9,11</sup> the existence of small domains/pockets in these media having viscosity quite different from the bulk viscosity is indeed consistent with literature.<sup>12</sup>

## 5. Concluding Remarks

Solvent mediated excited-state proton transfer reaction has been studied for the first time in RTILs employing 7-HQ, wherein the proton donor and acceptor groups are at some distance away and the proton transfer requires participation of the protic solvent molecules in an orderly manner. The results suggest that it is possible for the methanol molecules to form a bridged hydrogen-bonded architecture with 7-HQ in RTILs that is necessary for the proton relay in the system. The change in the kinetics of the ESPT process with methanol concentration has been attributed to a change of the viscosity of the medium. The lack of any proper correlation between the bulk viscosity and ESPT kinetics is attributed to the presence of micro/nano domains in RTILs having viscosity significantly different from the bulk viscosity.

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**Supporting Information Available:** Steady-state emission spectra of 7-HQ in neat RTILs and in presence of various concentrations of MeOH. The emission due to the neat RTILs under the identical instrumental settings is also available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Welton, T. *Chem. Rev.* **1999**, 99, 2071. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, 102, 3667. (c) *Ionic Liquids in Synthesis*; Welton, T., Wasserscheid, P., Eds.; VCH-Wiley: Weinheim, Germany, 2002. (d) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, 39, 3772. (e) *Ionic Liquids, Industrial Applications for Green Chemistry*; Rodgers, R., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002.
- (2) Huddleston, J. G.; Willauer, H. D.; Swatowski, R. P.; Visser, A. E.; Rodgers, R. D. *Chem. Commun.* **1998**, 1765.
- (3) (a) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. *J. Am. Chem. Soc.* **2004**, 126, 5300. (b) Dickinson, V. E.; Williams, M. E.; Hendrickson, S. M.; Masui, H.; Murray, R. W. *J. Am. Chem. Soc.* **1999**, 121, 613.
- (4) Seddon, K. R.; Stark, A.; Torres, M. J. In *Clean Solvents: Alternative Media for Chemical Reactions and Processing*; Abraham, M., Moens, L., Eds.; ACS Symposium Series 819; American Chemical Society: Washington, DC, 2002.
- (5) Samanta, A. *J. Phys. Chem. B* **2006**, 110, 13704.
- (6) Karmakar, R.; Samanta, A. *Chem. Phys. Lett.* **2003**, 376, 638.
- (7) Mandal, P. K.; Sarkar, M.; Samanta, A. *J. Phys. Chem. A* **2004**, 108, 9048.
- (8) Paul, A.; Samanta, A. *J. Phys. Chem. B* **2007**, 111, 1957.
- (9) Mandal, P. K.; Paul, A.; Samanta, A. *J. Photochem. Photobiol. A: Chem.* **2006**, 182, 113.
- (10) (a) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, 106, 4447. (b) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, 106, 6670. (c) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2003**, 107, 7340. (d) Saha, S.; Mandal, P. K.; Samanta, A. *Phys. Chem. Chem. Phys.* **2004**, 6, 3106. (e) Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, 109, 15172. (f) Paul, A.; Samanta, A. *J. Phys. Chem. B* **2007**, 111, 4724. (g) Paul, A.; Samanta, A. *J. Phys. Chem. B* **2008**, 112, 947.
- (11) (a) Padua, A. A. H.; Costa Gomes, M. F.; Lopes, J. N. A. C. *Acc. Chem. Res.* **2007**, 40, 1087. (b) Lopes, J. N. A. C.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, 110, 3330. (c) Triolo, A.; Russina, O.; Bleif, H.-J.; Di Cola, E. *J. Phys. Chem. B* **2007**, 111, 4641. (d) Shigeto, S.; Hamaguchi, H. *Chem. Phys. Lett.* **2006**, 427, 329. (e) Iwata, K.; Okazima, H.; Saha, S.; Hamaguchi, H. *Acc. Chem. Res.* **2007**, 40, 1174. (f) Xiao, D.; Rajian, J. R.; Cady, A.; Li, S.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem. B* **2007**, 111, 4669. (g) Jin, H.; Li, X.; Maroncelli, M. *J. Phys. Chem. B* **2007**, 111, 13473. (h) Hu, Z.; Margulis, C. J. *Acc. Chem. Res.* **2007**, 40, 1097. (i) Hu, Z.; Margulis, C. J. *Proc. Natl. Acad. Sci.* **2006**, 103, 831. (j) Wang, Y.; Jiang, W.; Yan, T.; Voth, G. A. *Acc. Chem. Res.* **2007**, 40, 1193. (k) Wang, Y.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, 127, 12192. (l) Adhikari, A.; Sahu, K.; Dey, S.; Ghosh, S.; Mandal, U.; Bhattacharyya, K. *J. Phys. Chem. B* **2007**, 111, 12809.
- (12) (a) Gutowski, K. I.; Japas, M. L.; Aramendia, P. F. *Chem. Phys. Lett.* **2006**, 426, 329. (b) Lu, J.; Liotta, C. L.; Eckert, C. A. *J. Phys. Chem. A* **2003**, 107, 3995.
- (13) (a) Tanner, C.; Manca, C.; Leutwyler, S. *Science* **2003**, 302, 1736. (b) Rini, M.; Magnes, B.-Z.; Pines, E.; Nibbering, E. T. J. *Science* **2003**, 301, 349. (c) Gutman, M.; Nachliel, E. *Annu. Rev. Phys. Chem.* **1997**, 48, 329. (d) Douhal, A.; Kim, S. K.; Zewail, A. H. *Nature* **1995**, 378, 260. (e) Lill, M. A.; Helms, V. *Proc. Natl. Acad. Sci. USA* **2002**, 99, 2778.
- (14) (a) Sengupta, P. K.; Kasha, M. *Chem. Phys. Lett.* **1979**, 68, 382. (b) MaMorrow, D.; Kasha, M. *J. Phys. Chem.* **1984**, 88, 2235.
- (15) Mason, S. F.; Philip, J.; Smith, B. E. *J. Chem. Soc.* **1968**, 3051.
- (16) Thistlethwaite, P. J.; Corkill, P. J. *Chem. Phys. Lett.* **1982**, 85, 317.
- (17) Thistlethwaite, P. J. *Chem. Phys. Lett.* **1983**, 96, 509.
- (18) Itoh, M.; Adachi, T.; Tokumara, K. *J. Am. Chem. Soc.* **1983**, 105, 4828.
- (19) Tokumara, K.; Itoh, M. *J. Phys. Chem.* **1984**, 88, 3921.
- (20) Itoh, M.; Adachi, T.; Tokumara, K. *J. Am. Chem. Soc.* **1984**, 106, 850.
- (21) Kwon, O.-H.; Lee, Y.-S.; Yoo, B. K.; Jang, D.-J. *Angew. Chem., Int. Ed.* **2006**, 45, 415.
- (22) Nakagawa, T.; Kohtani, S.; Itoh, M. *J. Am. Chem. Soc.* **1995**, 117, 7952.
- (23) Ochoa-G.; Bisht, P. B.; Sanchez, F.; Martinez-Ataz, E.; Santos, L.; Tripathi, H. B.; Douhal, A. *J. Phys. Chem. A* **1998**, 102, 8871.
- (24) Kohtani, S.; Tagami, A.; Nakagaki, R. *Chem. Phys. Lett.* **2000**, 316, 88.
- (25) Lavin, A.; Collins, S. *Chem. Phys. Lett.* **1993**, 207, 513.
- (26) (a) Douhal, A.; Sastre, R. *Chem. Phys. Lett.* **1994**, 219, 91. (b) Douhal, A.; Dabrio, J.; Sastre, R. *J. Phys. Chem.* **1996**, 100, 149. (c) Kwon, O.-H.; Doo, H.; Lee, Y.-S.; Jang, D.-J. *Chem. Phys. Chem.* **2003**, 4, 1079.
- (27) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, 35, 1168.
- (28) Paul, A.; Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, 109, 9148.
- (29) The viscosity of the ionic liquid was measured by a LVDV-III Ultra Brookfield cone and plate viscometer (1% accuracy and 0.2% repeatability).

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