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Chemical Physics Letters 415 (2005) 217–222

CHEMICAL PHYSICS LETTERS

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Excited-state proton transfer and excited-state de-hydrogen bonding of the push–pull styryl system

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Received 18 May 2005; in final form 14 August 2005
Available online 26 September 2005

Abstract

The excited-state reaction of push–pull styryl system was studied in this work. In the excited state, compounds of 2-StP-NMe$_2$, 2-StQ-NMe$_2$, 4-StQ-NMe$_2$ and 4-StP-NMe$_2$ possess a sufficiently large acidity change for the proton transfer process to occur. For compounds 2-StT-NMe$_2$ and 2-StN-NMe$_2$ the acidity change is too small to induce the proton transfer process. A new type of excited-state de-hydrogen bond (ESDHB) process was observed in this study. It is possible to explore the polarity and HB effect of solvent simultaneously by using the ESDHB mechanism.

1. Introduction

The photophysical aspects of intramolecular charge transfer (ICT) continue to attract attention for their importance in chemistry and biochemistry [1]. The ICT state often differs from the parent ground state in their geometry and electronic structure. For compounds such as push–pull stilbene system where the donor and the acceptor moiety are joined by a chemical bond the electron transfer occurs through a process called twisted intramolecular charge transfer (TICT) model [2]. For compounds with TICT, the dipole moment of the excited state is sensitive to the environment [2]. We have previously reported a study of excited-state deprotonation of *p*-*N*,*N*-dimethylamino-2-styrylquinoline (2-StQ-NMe$_2$) system [3]. There are two basic sites in 2-StQ-NMe$_2$, quinoline and *N*,*N*-dimethylaniline groups. The basicity of quinoline nitrogen atom is higher than the basicity of the *N*,*N*-dimethylaniline site. When the quinoline group is protonated, the absorption and emission peak shows a large red-shift. However, at a higher acid concentration the *N*,*N*-dimethylaniline group can accept a second proton which produces a large blue-shift at the absorption and emission peak. Since the basicity of the *N*,*N*-dimethylaniline group is reduced upon photoexcitation, the excited-state deprotonation (ESDP) process was observed in a doubly protonated form of 2-StQ-NMe$_2$ in dichloromethane solvent.

It is well known that the basicity of the acceptor will be increased and the basicity of the donor will be decreased upon photoexcitation because of the larger dipole moment in the excited state for ICT compounds [4,5]. This explains the ESDP of 2-StQ-NMe$_2$. However, the influence of various acceptors to the process of ESDP is still unknown. In this work compounds with different acceptors in a push–pull *p*-*N*,*N*-dimethylamino styryl system were synthesized to resolve this problem, as shown in Scheme 1.

Acid–base reactions generally follow a three-step mechanism:

$$\mathrm{B + H{-}A} \xrightleftharpoons{\text{association}} \underset{\text{HB}}{\mathrm{B\cdots HA}} \overset{\text{PT}}{\rightleftharpoons} \underset{\text{IP}}{\mathrm{BH^{+}\cdots A^{-}}} \xrightleftharpoons{\text{dissociation}} \underset{\text{free ions}}{\mathrm{Bh^{+} + A^{-}}}$$

where HB is a hydrogen bonding complex, IP is an ion-pair complex, and PT is proton transfer. Protons can be transferred from Brønsted acids (A–H) to bases (B) via hydrogen-bonds (HB) and ionic complexes (IP), depending

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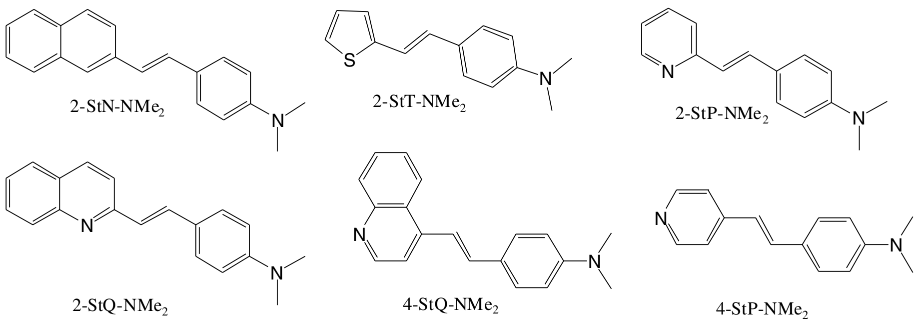
doi:10.1016/j.cplett.2005.08.146



Scheme 1.

on the relative acidity of H–A, the basicity of B, and the solvation capability of the surrounding medium [6,7]. The main factor, which determines the position of the acid/base equilibrium, is the differential solvation of the HB and IP complex. In dichloromethane protonation reaction will produce an IP complex because the solvation can not support the formation of free ions. The ESDP process forms a HB complex from an IP complex in the excited state [8–11]. Besides studying the influence of photoexcitation to a ground-state IP complex, we would like to study the influence of photoexcitation to a ground-state HB complex.

The influence of hydrogen-bonds (HB) to the absorption and emission maxima is usually less than protonation but in the same direction. Therefore, the HB interaction at an acceptor of an ICT compound causes a red-shift in the absorption and emission maxima, whereas the interaction at a donor site produces the opposite effect [12]. The extent of shift depends on the HB ability of solvent. The second part of this work will measure the spectra of 2-StN-NMe$_2$ in various ratios of dichloromethane and trifluoroethanol (TFE) solvents to explore the influence of photoexcitation to a ground-state HB complex.

The ultimate purpose of this work is to show the possibility of these compounds in probing of the microenvironment [13,14], which can detect the polarity and HB effect of interest at the same time [15,16].

2. Experimental

2.1. Materials

Compounds 2-StP-NMe$_2$, 4-StP-NMe$_2$, 2-StQ-NMe$_2$, and 4-StQ-NMe$_2$, were synthesized by reacting *p*-*N*,*N*-dimethylamino benzaldehyde with either α-picoline, γ-picoline, quinalide, or 4-methylquinoline. The mixture were refluxed in acetic anhydride catalyzed by zinc chloride for two to four hours [17]. The solid product was purified by column chromatography and recrystallized from ethyl acetate. 2-StT-NMe$_2$ and 2-StN-NMe$_2$ were prepared by Wittig condensation of *p*-*N*,*N*-dimethylamino benzaldehyde with 2-methylenethiophene or 2-methylenenaphthalene triethyl phosphonium ylides. The solid product was recrystallized from dichloromethane. All the solvents were Uvasol grade from Merk or spectrophotometric grade from Aldrich and were used as received.

2.2. Method

UV–Vis absorption spectra were recorded on a Perkin–Elmer Lambda 40 UV/Vis spectrometer and fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrometer. Sample with concentrations of 1.5×10^{-5} M were used for the measurements. The hydrochloric acid was dissolved in an ethyl acetate (EA) solution and was added to the organic phase at a volume of less than 3%. All acidic solvents were used when as fresh as possible.

3. Results and discussion

3.1. Factors which influence excited-state deprotonation

The absorption spectra and fluorescence spectra of compound 4-StP-NMe$_2$ in dichloromethane are shown in Fig. 1. In a neutral solution, the absorption and emission maxima of 4-StP-NMe$_2$ occurred at 363 and 457 nm, respectively, but were shifted to 456 and 560 nm, respectively after 5×10^{-5} M HCl was added. The pyridine nitrogen atom is more basic than the *N*,*N*-dimethylaniline site because of ICT. Therefore when the pyridine group is protonated, the electron pulling ability will be stronger and will show a larger red-shift in the absorption and emission spectra. When more acid was added, the double protonation induced an enormous blue-shift in the absorption and emission maxima. The absorption maxima shifted from 456 to 325 nm and the emission maxima (D band) shifted from 560 to 388 nm. Even though 4-StP-NMe2 became double protonated at higher acid concentration, the emission of a monoprotonated species (M band) is still very strong, as seen in Fig. 1. The similarities between the M band and the D band excitation spectra (data not shown) explain that these two emission bands are from the same source. The excitation spectra indicated that an ESDP process occurred at the *N*,*N*-dimethylaniline site. The basicity of *N*,*N*-dimethylaniline site was reduced upon photoexcitation. Besides 4-StP-NMe$_2$, the ESDP process was observed in double-protonated 2-StQ-NMe$_2$, 4-StQ-NMe$_2$ and 2-StP-NMe$_2$ in dichloromethane. However,

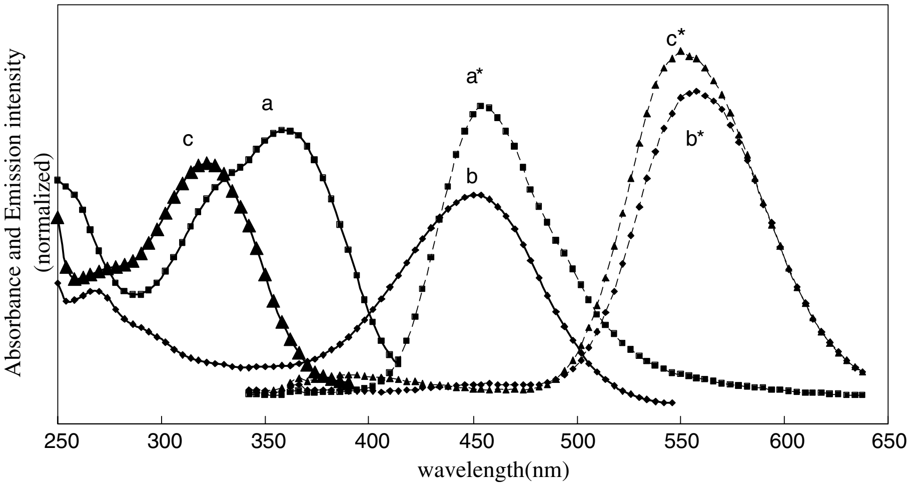


Fig. 1. The absorption and emission spectra of compound 4-StP-NMe$_2$ in dichloromethane under different conditions (solid line: absorption, dotted line: emission): (a) neutral solvent, (b) with 3.3×10^{-5} M HCl, (c) with 3.3×10^{-3} M HCl. (a*, b*, c* are emission spectra, EXC = 330 nm.)

compounds 2-StN-NMe$_2$ and 2-StT-NMe$_2$ displayed a different phenomenon.

The absorption and fluorescence spectra of compound 2-StN-NMe$_2$ in dichloromethane are shown in Fig. 2. The absorption maxima shows a blue-shift from 367 to 323 nm and the emission maxima blue-shifts from 460 to 391 nm when HCl is added to the solution. Unlike 4-StP-NMe$_2$, our experiments did not produce ESDP in 2-StN-NMe$_2$. Compounds 2-StT-NMe$_2$ and 2-StN-NMe$_2$ exhibit similar behavior. For ICT compounds, the basicity of the donor decreases upon photoexcitation due to the larger dipole moment in the excited state.

By using of the Forster cycle the excited-state acidity constant ($\mathrm{p}K_\mathrm{a}^*$) can be predicted from the ground-state ($\mathrm{p}K_\mathrm{a}$) value and the excitation energy difference ($E_{\mathrm{A}^-} - E_{\mathrm{AH}}$) between the unprotonated and protonated forms by the following equation [18]

$$\mathrm{p}K_\mathrm{a}^* = \mathrm{p}K_\mathrm{a} + (E_{\mathrm{A}^-} - E_{\mathrm{AH}})/2.3RT, \quad (1)$$

$$\Delta \mathrm{p}K_\mathrm{a} = \mathrm{p}K_\mathrm{a}^* - \mathrm{p}K_\mathrm{a} = (E_{\mathrm{A}^-} - E_{\mathrm{AH}})/2.3RT. \quad (2)$$

The basicity difference between the excited state and ground state ($\Delta \mathrm{p}K_\mathrm{a}$) of different compounds is listed in Table 1. Compounds of 2-StP-NMe$_2$, 2-StQ-NMe$_2$, 4-StQ-NMe$_2$ and 4-StP-NMe$_2$ which show ESDP processes possess a large value of $\Delta \mathrm{p}K_\mathrm{a}$, For compounds without ESDP process, such as 2-StT-NMe$_2$ and 2-StN-NMe$_2$, the value of $\Delta \mathrm{p}K_\mathrm{a}$ is smaller. The ESDP process was induced by a large change in basicity between the ground state and the excited state. For compounds 2-StT-NMe$_2$ and 2-StN-NMe$_2$, the value of $\Delta \mathrm{p}K_\mathrm{a}$ is too small to induce the ESDP process from the protonated species. Therefore, we conclude that the value of $\Delta \mathrm{p}K_\mathrm{a}$ is important in determining the occurrence of ESDP process.

3.2. Excited-state de-hydrogen bonding

The absorption and emission spectra of compound 2-StN-NMe$_2$ in various ratios of mixed solvents between dichloromethane and trifluoroethanol (TFE) are shown in Fig. 3. The absorption maxima displayed a blue-shift when

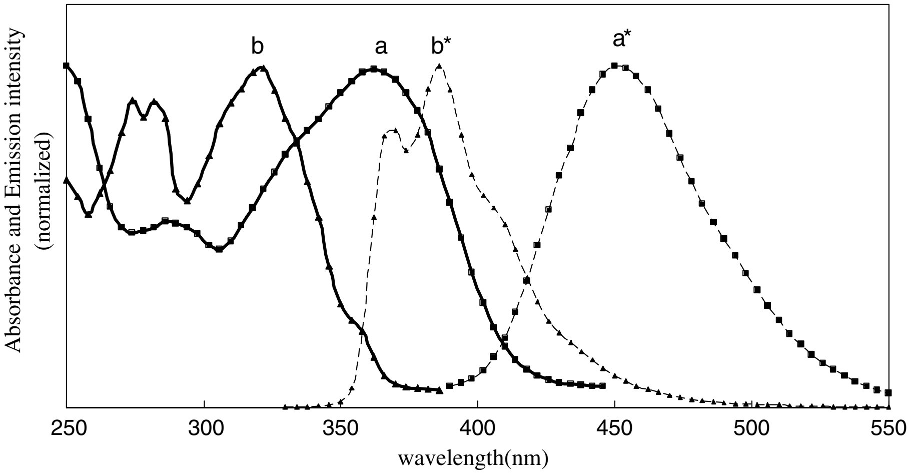


Fig. 2. The absorption and emission spectra of compound 2-StN-NMe$_2$ in dichloromethane under different conditions (solid line: absorption, dotted line: emission): (a) neutral solvent, (b) with 2.2×10^{-3} M HCl. (a*, b* are emission spectra, EXC = 320 nm.)

Table 1
The absorption maxima and the basicity difference between the excited state and the ground state (ΔpK_a) of unprotonated (A^-) and protonated (AH) forms of different compounds in water

Compound	E_{A^-} (nm) Absorption maxima	E_{AH} (nm) Absorption maxima	ΔpK_a[a]
2-StN-NMe_2	344.5	317.5	−5.2
2-StT-NMe_2	346.5	323.5	−4.3
2-StQ-NMe_2	485.0	366.0	−14.0
2-StP-NMe_2	428.0	324.5	−15.6
4-StQ-NMe_2	494.5	365.0	−15.1
4-StP-NMe_2	444.5	320.5	−18.3

[a] Basicity difference between the excited state and the ground state.

the ratio of TFE in the mixed solvent was increased, whereas the emission maxima exhibited an opposite behavior. Since TFE is a protic solvent, it is reasonable to conclude that hydrogen-bonds form between the *N*,*N*-dimethylaniline site (donor site) of compound 2-StN-NMe_2 and the solvent molecules. Therefore, the absorption maxima displayed a blue-shift when the ratio of TFE is increased in the mixed solvent. However, it was found that the emission maxima exhibited a red-shift instead of a blue-shift. This phenomenon can be explained by the ground-state hydrogen bonding complex practicing a excited-state de-hydrogen bonding (ESDHB) process because of the basicity of *N*,*N*-dimethylaniline site decreasing upon photoexcitation. The influence of the HB effect was counteracted in the excited state, so the emission maxima was dominated by solvent polarity. An increase in polarity stabilizes the ICT state by solvation, hence the emission maxima undergoes a red-shift with an increase of solvent polarity. Since the polarity of TFE is higher than dichloromethane, the emission maxima displays a red-shift with an increase of the solvents polarity when ESDHB occurs in the excited state.

In order to counteract the influence of protonation, a large quantity (0.01 M) of triethylamine was added. If protonation occurred in 2-StN-NMe_2 the addition of triethylamine induced a deprotonation process, which produced an obvious change in absorption and emission spectra [12]. Neither the absorption nor the emission spectra of the 2-StN-NMe_2 were affected by the presence of triethylamine. Therefore, the influence of TFE to 2-StN-NMe_2 is seen mainly the HB interaction.

The reaction barrier of the proton transfer is higher than the ESDHB process. The value of ΔpK_a for 2-StN-NMe_2 is not enough to stimulate the occurrence of ESPT, but for the ESDHB process, the smaller reaction barrier of the ESDHB process can be observed in this study.

3.3. Solvatochromism of 2-StN-NMe_2

It is well known that solvent-dependent spectral shifts occur from either general or specific solvents effects. The first effect is the interaction of the fluorophore with the reactive field induced by the surrounding solvent. Specific effects result from the short-range interaction between the fluorophore with one or more solvent molecules [18,19], such as the hydrogen bond. Generally speaking, the Stokes shift of the ideal chromophore is supposedly determined by only nonspecific solvation. However, the interactions from HB are known to lead to deviations from ideal polarity correlation. To distinguish between the two effects, it is important to quantify the relative contribution from these two effects. For compounds with acidic (or basic) sites, it is difficult to separate these two effects when the solvent is a hydrogen bond acceptor, or hydrogen bond donor. Therefore, it is our goal to find a fluorophore that can simultaneously measure nonspecific and specific effects, such as HB effects.

The HB interaction of 2-StN-NMe_2 in the ground state will exhibit a blue-shift at absorption maxima, but the ESDHB process will counteract this influence. The value of the blue-shift in the absorption maxima was influenced by HB, but the emission maxima only responded to pure nonspecific interaction. Thus, 2-StN-NMe_2 will produce a large Stokes'-shift fluorescence in a hydrogen-bond solvent.

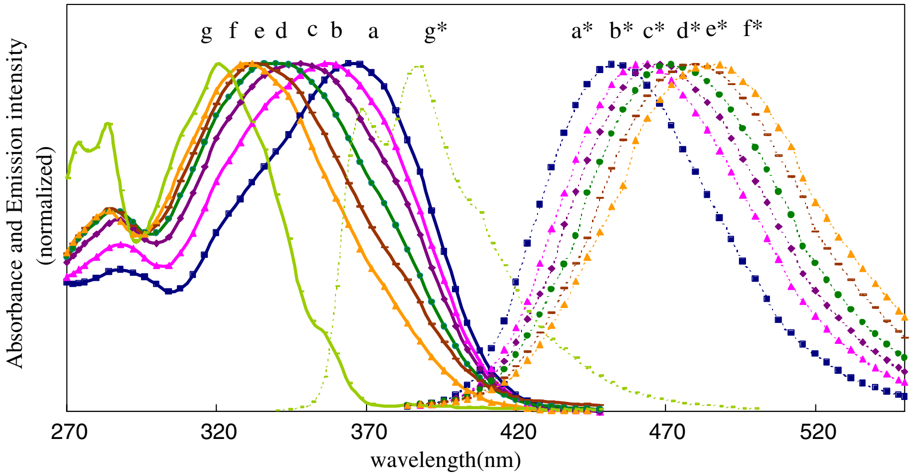


Fig. 3. The absorption and emission spectra of compound 2-StN-NMe_2 in different mixed solvents (v/v_0) between CH_2Cl_2 and CF_3CH_2OH. (solid line: absorption, dotted line: emission): (a) CH_2Cl_2 100%, (b) CH_2Cl_2 80%, (c) CH_2Cl_2 60%, (d) CH_2Cl_2 40%, (e) CH_2Cl_2 20%, (f) CH_2Cl_2 0%, (g) with 1.0×10^{-3} M HCl in CH_2Cl_2 (a*, b*, c*, d*, e*, f*, g* are emission spectra, EXC = 340 nm.).

The absorption maxima and emission maxima of 2-StN-NMe$_2$ in different solvents are collected in Table 2. It is seen that the absorption maxima does not vary with different solvents. Although the absorption maxima was insensitive to solvent polarity, the emission maxima showed a significant bathochromic shift with increasing solvent polarity. The relationship between the Stokes shift of 2-StN-NMe$_2$ to different solvent polarity are shown in

Table 2
The absorption and emission maxima of compound 2-StN-NMe$_2$ in different solvents

Solvent	f_ε[a]	α-Scale[b]	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Stokes shift (cm^{-1})	Pure HB effect (cm^{-1})
n-Hexane	0.1849		356.6	409.2	3604	
Cyclohexane	0.2023		358.2	413.8	3751	
Toluene	0.2396		365.4	430.0	4111	
Di-*n*-butyl ether	0.2905		359.8	424.4	4230	
Diethyl ether	0.345		359.0	432.4	4728	
Ethyl acetate	0.385		362.2	448.4	5308	
THF	0.4072		364.6	455.6	5478	
CH_2Cl_2	0.4156		367.0	460.0	5509	
Acetone	0.4646		363.0	471.8	6353	
DMF	0.480		367.0	478.6	6354	
CH_3CN	0.4803		363.0	477.8	6619	
DMSO	0.4841		371.8	490.0	6488	
Ethanol	0.47	0.86	359.8	458.8	5997	−274
Ethylene glycol	0.4803	0.9	364.2	477.8	6528	153
Methanol	0.4774	0.98	359.0	472.2	6678	334
Glycerol	0.484	1.21	333.5	477.2	9029	2620
Trifluoroethanol	0.4724	1.51	328.6	497.6	10336	4041

Acronyms. Tetrahydrofuran (THF), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO).

[a] $f(\varepsilon)$, Kirkwood function ($= (\varepsilon - 1)/(2\varepsilon + 1)$); ε, dielectric constant.

[b] Hydrogen-bond acidity [20].

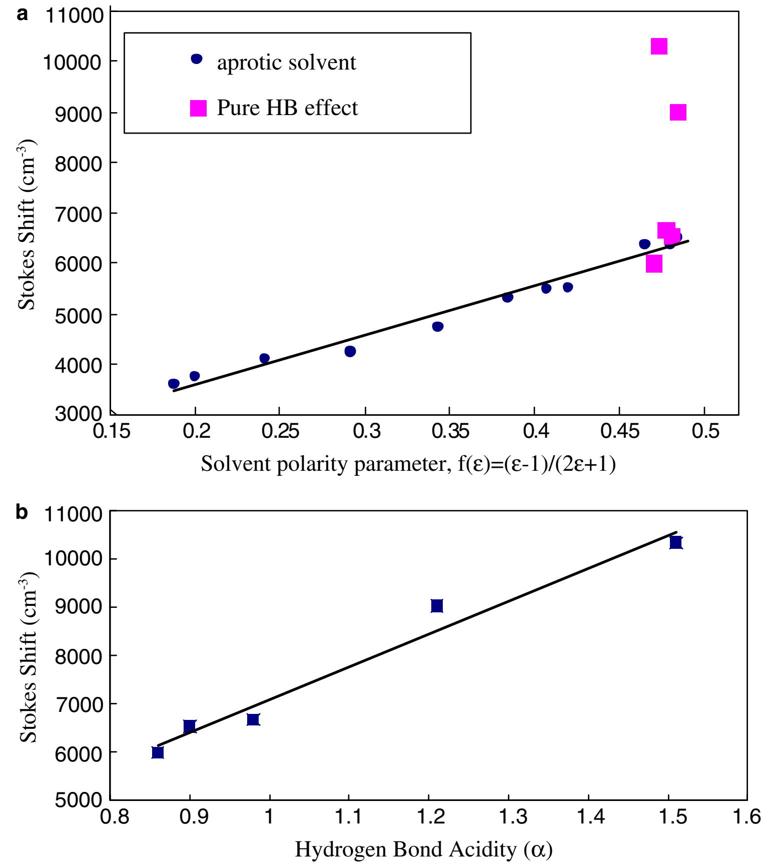


Fig. 4. The relationship between the Stokes shift of compound 2-StN-NMe$_2$ to different solvent polarity function. (a) Kirkwood function ($f_\varepsilon = (\varepsilon - 1)/(2\varepsilon + 1)$). (b) Hydrogen bond acidity.

Fig. 4. For an aprotic solvent the Kirkwood function ($f_\varepsilon = (\varepsilon - 1)/(2\varepsilon + 1)$), a solvation scale to measure nonspecific interaction, is used in Fig. 4a. For a protic solvent the hydrogen bond acidity, α, developed by Taft is used to explore the influence of HB to the Stokes shift [20]. A good linear correlation exists between the Stokes shift (cm^{-1}) and different solvent polarity functions, except for the protic solvent, as seen in Fig. 4a. But in Fig. 4b, a good linear correlation exists between the Stokes shift and hydrogen bond acidity. The correlation indicates that nonspecific interaction possesses a dominant importance in aprotic solvents, but HB interactions do exist between 2-StN-NMe$_2$ molecules and protic solvents.

The value of the Stokes shift obtained in protic solvents was higher than the one measured in aprotic solvents. The HB interaction between *N*,*N*-dimethylaniline site and protic solvents was stronger in the ground state, leading to hypsochromic shifts in the absorption maxima with increasing α. This bond breaks after photoexcitation, so the emission maxima are not seriously influenced by the HB interaction, resulting in a large Stokes shift.

By calculating the deviation from linearity of protic solvents, we can quantify the influence of HB, as shown in Fig. 4a. These values are listed in Table 2. Unlike the protonation effect, the steric effect is significant for HB interactions [12]. Table 2 shows that the HB interaction contributes a positive Stokes shift only when the hydrogen bond acidity is higher than the ethylene glycol. This means that the ground-state HB interaction is not important for ethanol because of its lower HB acidity and its bulky steric effect.

4. Conclusion

Compounds of 2-StP-NMe$_2$, 2-StQ-NMe$_2$, 4-StQ-NMe$_2$, and 4-StP-NMe$_2$, which possesses a large value of ΔpK_a practice the proton transfer process in the excited state. For compounds 2-StT-NMe$_2$ and 2-StN-NMe$_2$, the value of ΔpK_a is too small to induce the ESDP process. Thus only an ESDHB process, which possesses a smaller reaction barrier than ESDP, was observed in this study. Using this mechanism, we can probe the polarity and HB effect of an interesting microenvironment at the same time.

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