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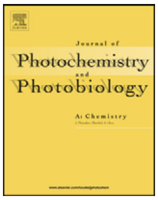

Influences of protonation and hydrogen bonding on intramolecular charge transfer compounds possessing different spacers

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ABSTRACT

This work investigated the influence of protonation and hydrogen bonding on intramolecular charge transfer (ICT) through different spacers. Three compounds, DS-NH_2 (with a conjugated double bond), TS-NH_2 (with a conjugated triple bond), and SS-NH_2 (with a flexible saturated bond), possessing the same donor group (aniline) and the same acceptor group (naphthalene) but with different linkages were synthesized for this purpose. The double bond and triple bond spacers provided a more efficient ICT pathway than a flexible saturated bond in the ground state, so an ICT absorption band was observed for compounds DS-NH_2 and TS-NH_2. Although SS-NH_2 did not exhibit any ICT absorption band, two kinds of intramolecular exciplex emissions were observed depending on the solvent polarity. The excited-state dipole moment of DS-NH_2 is less than that of TS-NH_2. The ICT absorption and emission bands are quenched by protonation in this system. The influence of hydrogen bonding for DS-NH_2 and TS-NH_2 only occurs in the ground state and disappears in the excited state. The intermolecular hydrogen-bond between SS-NH_2 and CF_3CH_2OH molecules block the reorientation of the amino group and prevent the occurrence of the ICT. Therefore, no exciplex emission was recorded for SS-NH_2 in the mixed (CH_2Cl_2:CF_3CH_2OH) solvents.

1. Introduction

Intramolecular charge transfer (ICT) reaction is important to the natural and material sciences yet complex [1–4]. To better understand this process, researchers have utilized a simplified model to study influential factors which include donor–acceptor distance, orientation [5–10], and substituent effects on ICT reactions [11–15]. Compounds consisting of donor–acceptor chromophoric species linked by a spacer are often used for this purpose [16,17].

ICT reactions can be strongly influenced by the nature of the spacer intervening between the donor and the acceptor [18]. The occurrence of an ICT reaction can pass through a saturated (flexible or rigid) [19] or unsaturated (conjugated or peptide bond) spacer [20]. Different linkages including C-C single bond, C-C double bond [21,22], C-C triple bond [23,24], S-S bond [25], amide bond [26,27], and thiophene ring [28] were used as spacers to study the linkage efficiency for ICT reactions. However, relatively little is known about the influence of intermolecular interactions, specifically protonation and hydrogen bonding, on an ICT reaction through different spacers [29–31].

In this work, three compounds, SS-NH_2, DS-NH_2, and TS-NH_2 (Scheme 1) were synthesized to study the influence of protonation or hydrogen bonding on an ICT reaction using different spacers. These compounds possess the same donor group (aniline) and same acceptor group (naphthalene) but have different linkages. We found that the conjugated double bond and the conjugated triple bond are both effective in charge transfer but they produce different localized orbitals at the donor and acceptor fragments. Moreover, the ICT reaction through these linkages is strongly influenced by the intermolecular interactions.

2. Experimental

Compound DS-NH_2 (*p*-amino-2-*trans*-styrylnaphthalene) was synthesized through Wittig condensation of *p*-nitro benzaldehyde with 2-methylenenaphthalene triphenyl phosphonium ylide. Then, the nitro-product (*p*-nitro-2-*trans*-styryl naphthalene) was reduced by hydrogenation under Sn and aqueous HCl. If the hydrogenation reaction was preceded by Pd/C and hydrogen gas in methanol, then the product was SS-NH_2 (1-(*p*-aniline)-2-(2-naphthyl) ethane). Compound TS-NH_2 (1-(*p*-aniline)-2-(2-naphthyl) ethyne) was obtained after three steps from *p*-nitro-2-*trans*-styrylnaphthalene: step 1 involved the formation of a dibromo product by using bromine water in $CHCl_3$; in step 2, the dibromo product was treated with potassium *tert*-butoxide

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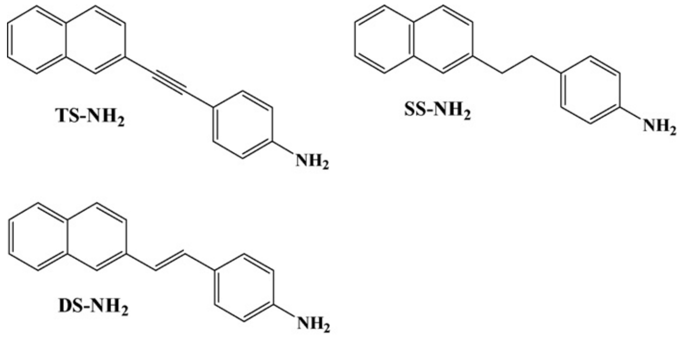


Scheme 1. The structure of compounds TS-NH$_2$, SS-NH$_2$, and DS-NH$_2$.

under THF refluxing to produce an ethynyl compound; and step 3 consisted of the hydrogenation of nitro to amino by Sn and aqueous HCl. All of the products were purified by column chromatography and recrystallized from the mixed solvents between ethyl acetate and *n*-hexane (more details are shown in Supporting information).

All calculations were made by using the *Spartan* software package. The most stable conformations were searched by single-point calculation using the semi-empirical method (PM3) by way of rotating the bonds systematically. Torsion angles of these bonds were varied with a 30° step while other geometrical parameters were fixed. Finally, the most stable conformers were fully optimized without any constraints using the 6-31G* basis set (*ab initio* molecular orbital). All of the fully optimized structures were confirmed to exhibit the minimum energy structures by frequency calculations (none of imaginary frequency).

Quinine sulfate in 1 N sulfuric acid ($\Phi_f = 0.546$) was used as a standard for the fluorescence quantum yield determinations [32]. All solvents were Uvasol grade from Merck or spectrophotometric grade from Aldrich and were used as received. UV–Vis absorption spectra were recorded on a Hitachi U-3010 spectrometer and fluorescence spectra were obtained using a Hitachi F-4500 fluorescence spectrometer. Samples with concentrations of 1.5×10^{-5} M were used for the measurements.

3. Results

3.1. Spacer effects on intramolecular charge transfer

The absorption and emission spectra of compounds SS-NH$_2$, DS-NH$_2$, and TS-NH$_2$ in CH$_3$CN are shown in Fig. 1. The excitation spectra match the absorption spectra for compounds SS-NH$_2$, DS-NH$_2$, and DS-NH$_2$ (shown in Supporting information). The absorption spectrum of SS-NH$_2$ is virtually identical with a superposition of those having separate chromophores of SS-NH$_2$, naphthalene and aniline, implying a lack of significant electronic interaction between naphthalene and aniline. However, the absorption spectrum of DS-NH$_2$ displays a broad band, located at about 347 nm, which cannot be reproduced by a superposition of those having separate chromophores of DS-NH$_2$. This band is a typical ICT band. The ICT band was also observed through the absorption spectrum of TS-NH$_2$. These results indicate that a strong electronic interaction existed between the donor and acceptor for DS-NH$_2$ and TS-NH$_2$.

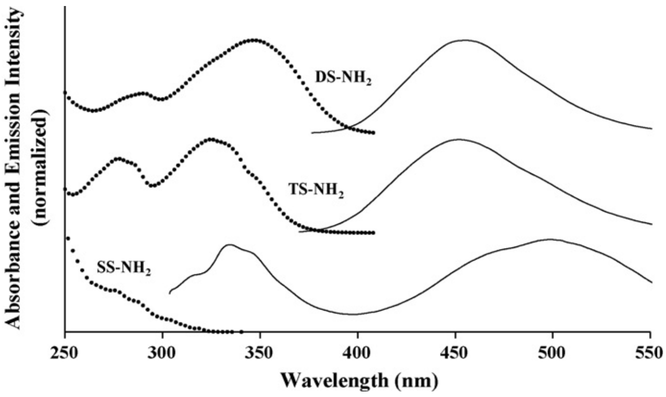


Fig. 1. The absorption and emission spectra of SS-NH$_2$ (EXC = 290 nm), DS-NH$_2$ (EXC = 350 nm), and TS-NH2 (EXC = 335 nm) in CH$_3$CN (dot line: absorption, black line: emission).

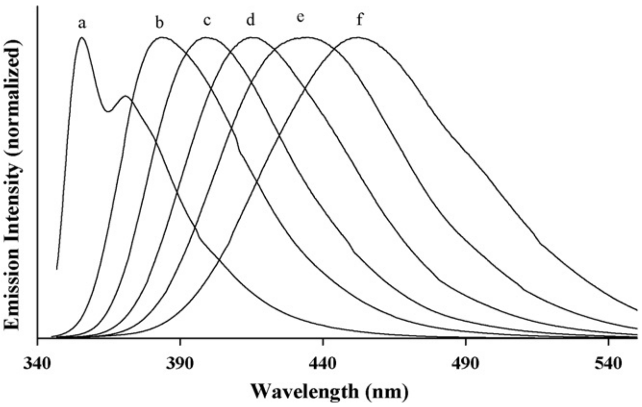


Fig. 2. The emission spectra of compound TS-NH$_2$ in different solvents. (EXC = 335 nm): (a) cyclohexane (CHX), (b) CHX90EA10 (EA: ethyl acetate), (c) CHX60EA40, (d) EA, (e) EA80ACN20, and (f) CH$_3$CN (ACN).

Two separated emission bands are observed for SS-NH$_2$ in Fig. 1. The excitation spectra for the two emission bands are almost same. The fine-structure fluorescence between 320 nm and 360 nm, assigned as the LE band, is a characteristic of naphthalene. Since there is no detectable ground-state complex for SS-NH$_2$ in Fig. 1, the huge Stokes shift for SS-NH$_2$ (more than 14,000 cm^{-1} in CH$_3$CN) cannot be explained by the solvent relaxation. We regard an excited-state complex was formed after photoexcitation and the broad band peaking at about 500 nm is seen as an emission from an intramolecular exciplex. The emission spectra of both DS-NH$_2$ and TS-NH$_2$ display a broad emission band, a typical emission from an ICT state.

The emission spectra of TS-NH$_2$ and SS-NH$_2$ in different solvents are shown in Figs. 2 and 3, respectively. The absorption and emission maxima of SS-NH$_2$, DS-NH$_2$, and TS-NH$_2$ are listed in Table 1. The absorption maxima of DS-NH$_2$ and TS-NH$_2$ are not sensitive to the solvent polarity but the fluorescence spectra of these two

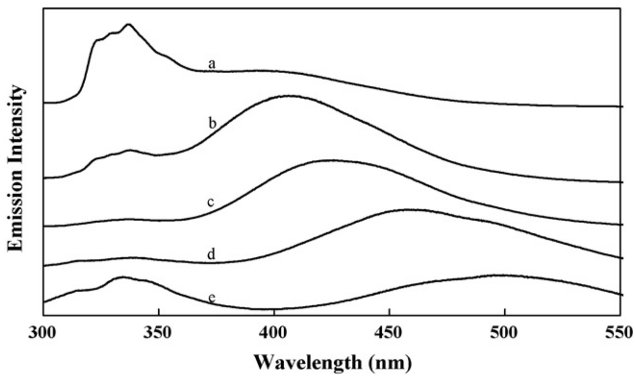


Fig. 3. The emission spectra of compound SS-NH$_2$ in different solvents (EXC = 290 nm): (a) CHX90EA10, (b) CHX60EA40, (c) EA, (d) EA80ACN20, and (e) CH$_3$CN.

Table 1
The absorption and emission maxima, quantum yield of DS-NH_2, TS-NH_2 and SS-NH_2 in different solvents.

Solvent	Δf	Δf_{ex}	DS-NH_2		TS-NH_2		SS-NH_2			
			λ_{max}^{UV} (nm)	$\lambda_{max}^{F}(\varphi)^a$ (nm)	λ_{max}^{UV} (nm)	$\lambda_{max}^{F}(\varphi)^a$ (nm)	$\lambda_{max}^{LE}(\varphi)^a$ (nm)	$\lambda_{max}^{EX}(\varphi)^a$ (nm)	EX(φ) + LE(φ)	EX(φ)/LE(φ)
CHX	−0.004	0.098	340	394 (0.097)	322	356	337 (0.13)		0.13	0
$CHX_{90}EA_{10}$	0.039	0.140	344	413 (0.062)	324	384 (0.76)	337 (0.043)	395 (0.050)	0.093	1.2
$CHX_{70}EA_{30}$	0.099	0.198	347	422 (0.044)	325	396 (0.64)	338 (0.011)	405 (0.077)	0.088	7.0
$CHX_{60}EA_{40}$	0.120	0.219	347	425 (0.031)	325	399 (0.59)	337 (0.0064)	409 (0.070)	0.076	10.9
$CHX_{40}EA_{60}$	0.154	0.250	348	430 (0.051)	325	407 (0.54)	338 (0.0033)	415 (0.068)	0.071	20.6
$CHX_{20}EA_{80}$	0.179	0.274	348	430 (0.050)	325	412 (0.48)	338 (0.0023)	419 (0.063)	0.065	27.4
EA	0.199	0.292	348	437 (0.047)	325	415 (0.45)	337 (0.0014)	426 (0.062)	0.063	44.3
$EA_{95}ACN_5$	0.222	0.315	348	439 (0.049)	325	419 (0.42)	337 (0.0032)	446 (0.046)	0.049	14.4
$EA_{90}ACN_{10}$	0.238	0.330	348	442 (0.043)	325	425 (0.40)	338 (0.0037)	453 (0.042)	0.046	11.4
$EA_{80}ACN_{20}$	0.258	0.350	348	448 (0.046)	325	434 (0.35)	338 (0.0030)	460 (0.031)	0.034	10.3
$EA_{60}ACN_{40}$	0.279	0.370	348	449 (0.034)	325	444 (0.32)	338 (0.0031)	473 (0.022)	0.025	7.1
ACN	0.305	0.392	347	456 (0.043)	325	452 (0.24)	335 (0.0045)	500 (0.0098)	0.014	2.2
MeOH	0.308	0.393	341	458 (0.043)	324	451 (0.011)	337 (0.0045)	505 (0.0012)	0.0057	0.3
TFE	0.283	0.378	325	468 (0.053)	321	452 (0.015)	336 (0.015)		0.015	0

[a] Fluorescence quantum yield. CHX: cyclohexane; EA: ethyl acetate; ACN: CH_3CN; $CHX_{90}EA_{10}$: 90% CHX and 10% EA (v/v).

compounds display a bathochromic shift in polar solvents. This is a typical phenomenon for an emission from an ICT state. The LE emission maxima of SS-NH_2 are independent on the solvent polarity. However, the exciplex emission maxima of SS-NH_2 display a bathochromic shift in polar solvents. The fluorescence quantum yield (ϕ_F) of TS-NH_2 is larger than that of DS-NH_2 by 1 order of magnitude and reduces with increasing solvent polarity. The ϕ_F values of TS-NH_2 are more sensitive to the solvent polarity than that of DS-NH_2.

The emission spectra of SS-NH_2 strongly depend on the solvent polarity. In cyclohexane, only the LE emission is observed. The LE emission decreases and the exciplex emission appears when the polarity of solvent increases. The values of ratio (exciplex (ϕ_F)/LE (ϕ_F)) reach a maximum in a moderately polar solvent (EA) and decrease at higher solvent polarity.

The dipole-moment difference between a ground state and an excited state for a compound with ICT characteristics can be estimated from the slope of Stokes shift vs. solvent polarity parameter Δf (Lippert–Mataga equation) [33]:

$$\Delta\nu = \nu_{abs} - \nu_f = \left(\frac{2\ \Delta\mu^2}{hc\rho^3}\right)\Delta f + \text{constant} \tag{1}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

where $\Delta\nu$ is the Stokes shift (in cm^{-1}); ν_{abs} and ν_f are the absorption maxima and emission maxima (in cm^{-1}), respectively; h is Planck's constant, c is the speed of light, ρ is the Onsager cavity radius of the molecule, $\Delta\mu = \mu_e - \mu_g$ is the dipole moment difference between the ground state (μ_g) and the excited state (μ_e), ε is the dielectric constant, and n is the refractive index.

According to Mataga et al., the excited-state dipole moment of an exciplex can also be estimated from the solvatochromic shift of the emission maxima using a similar equation [34]:

$$\nu_{ex} = \nu_{ex}^{o} - \left(\frac{2\mu^2}{hc\rho^3}\right)\Delta f_{ex} \tag{3}$$

$$\Delta f_{ex} = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \tag{4}$$

where ν_{ex} is the emission maximum (in cm^{-1}) of an exciplex in a given solvent, ν_{ex}^{o} is the emission maximum (in cm^{-1}) in the gas phase, and μ is the dipole moment of the exciplex.

The Stokes-shift values for DS-NH_2 and TS-NH_2 are plotted against Δf in Fig. 4a. The calculated ground-state dipole moment of DS-NH_2 and TS-NH_2 are the same and equal to 2.0D. The Onsager radius was taken as 7.0×10^{-10} m (40% of the major axis of the molecule) for SS-NH_2, DS-NH_2 and TS-NH_2. The excited-state dipole moments for DS-NH_2 and TS-NH_2 calculated by the slopes in Fig. 4a were 18D and 24D, respectively. It is worth to mention that the emission maxima plotted against Δf for DS-NH_2 and TS-NH_2 also displayed a linear relationship because the absorption maxima for DS-NH_2 and TS-NH_2 are not very sensitive to the solvent polarity. The high values of μ_e show that a significant ICT reaction occurs for DS-NH_2 and TS-NH_2 in the excited state. The emission maxima of the exciplex for SS-NH_2 are plotted against Δf_{ex} in Fig. 4b. Two different slopes can be observed from the plot of ν_{ex} vs. Δf_{ex} in Fig. 4b. The slope of the solvatochromic plot

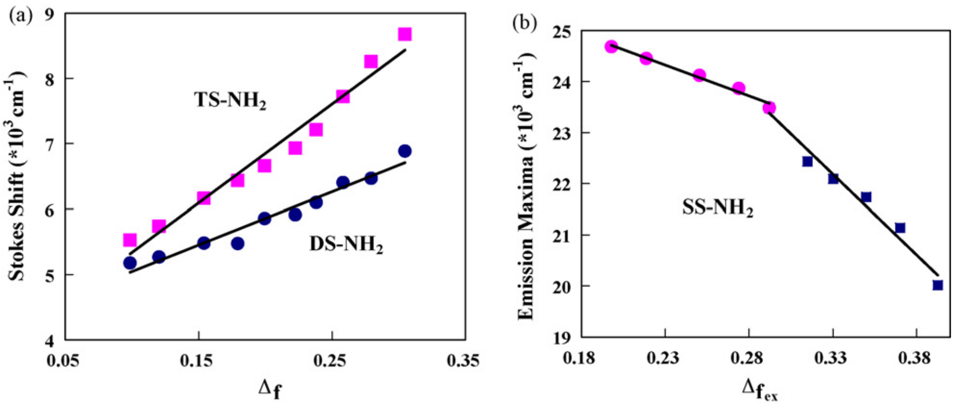


Fig. 4. Plot of stokes shift or emission maxima against the solvent polarity Δf or Δf_{ex}. (a) Stokes shift against Δf for DS-NH_2 and TS-NH_2 and (b) emission maxima against Δf_{ex} for SS-NH_2.

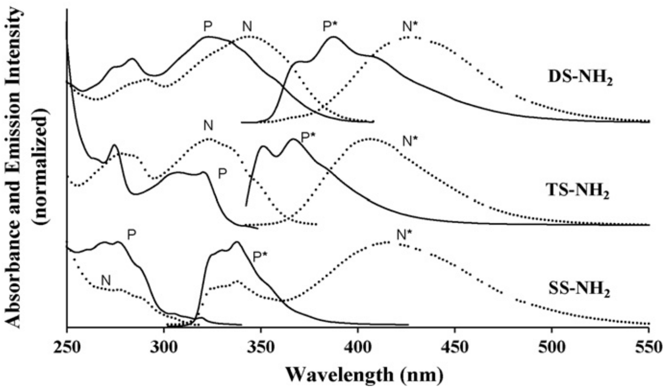


Fig. 5. The absorption and emission spectra of SS-NH_2, DS-NH_2 and TS-NH_2 in neutral or acidic CH_2Cl_2 solution (acidic by CF_3COOH) (dot line: neutral solution (N); black line: after protonation (P); N and P are absorption spectra, N* and P* are emission spectra).

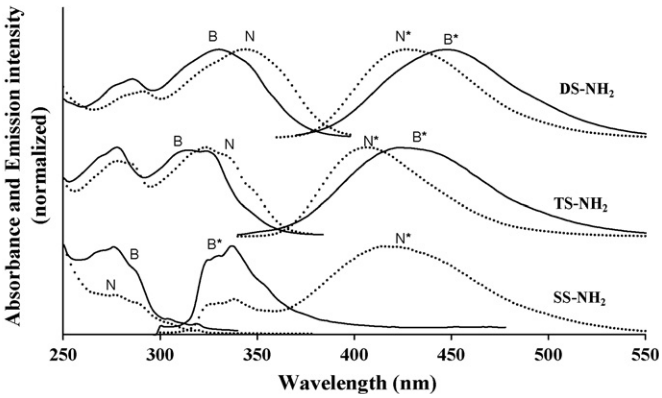


Fig. 6. The absorption and emission spectra of SS-NH_2, DS-NH_2 and TS-NH_2 in CH_2Cl_2 and mixed solvents (CH_2Cl_2:CF_3CH_2OH = 3:2) (dot line: pure CH_2Cl_2, (N); black line: mixed solvent, (B); N and B are absorption spectra, N* and B* are emission spectra).

is much steeper in the polar solvents than in the non-polar solvents. From the Lippert–Mataga plot in the non-polar solvents, i.e., from $CHX_{70}EA_{30}$ to EA, one could calculate the excited-state dipole moment of SS-NH_2 is 20D. The excited-state dipole moments of SS-NH_2 determined from the polar solvents (the solvent polarity exceeds EA) resulted in a much bigger value, 33D.

3.2. *Protonation effects*

Protonation influence on the absorption and emission spectra of SS-NH_2, DS-NH_2, and TS-NH_2 in CH_2Cl_2 are shown in Fig. 5. The absorption and emission maxima for DS-NH_2 and TS-NH_2 all display a blue-shift after protonation by CF_3COOH. The fine-structure fluorescence spectrum in Fig. 5 implies the disappearance of emission from an ICT state. The absorption spectrum of SS-NH_2 displays little change after protonation except for some background absorption from CF_3COOH. The exciplex emission of SS-NH_2 disappears after protonation and only the LE emission is observed in the fluorescence spectra.

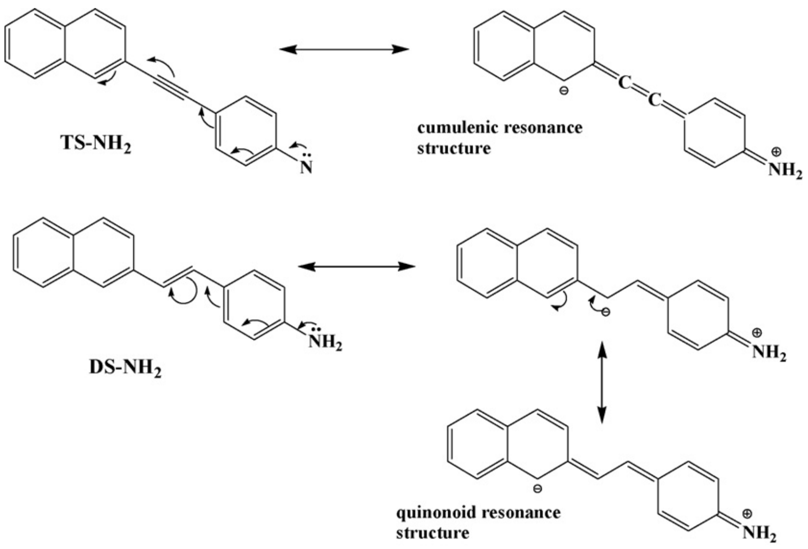
3.3. *Hydrogen-bond effects*

The absorption and emission spectra for SS-NH_2, DS-NH_2, and TS-NH_2 in CH_2Cl_2 and in CH_2Cl_2–CF_3CH_2OH (60:40) mixed solvents are shown in Fig. 6. Compared with pure CH_2Cl_2, compounds DS-NH_2 and TS-NH_2 show a blue-shift in the absorption maxima but exhibit a red-shift in the emission maxima in mixed solvents. The absorption spectrum of SS-NH_2 displays little change after the addition of CF_3CH_2OH molecules except for some background absorption from CF_3CH_2OH. Interestingly, there is only an LE emission band observed in the emission spectra of SS-NH_2 in Fig. 6. It is obvious that the hydrogen-bond formation between SS-NH_2 and CF_3CH_2OH molecules results in a significant influence on the emission spectra of SS-NH_2.

4. Discussion

The magnitude of a donor–acceptor electronic coupling is proportional to both the orbital overlap of the spacer-donor and the spacer-acceptor. A double bond or a triple bond spacer provides an efficient pathway for donor–acceptor interaction through a conjugated framework. Therefore, an ICT absorption band is observed for DS-NH_2 and TS-NH_2 (Fig. 1). The results indicate that a strong electronic interaction happens between naphthalene and aniline through a conjugated spacer in the ground state.

It is interesting to note that the excited-state dipole moment of TS-NH_2 (24D) is larger than that of DS-NH_2 (18D). Delocalization of charge along the π system through an acetylene linkage includes



Scheme 2. The resonance structure of TS-NH_2 and DS-NH_2.

a cumulenic resonance structure, as shown in Scheme 2. But for an ethylenic linkage, a quinonoid resonance structure (Scheme 2) might be expected to result from the migration of charges. The quinonoid structure occurring in the transfer process might localize a negative charge on the carbon atom of the spacer and reduce the excited-state dipole moment [35]. The localized charge at the spacer has been used to explain the regioselectivity of methanol addition to 2-(*meta*-aminostyryl) naphthalene [36]. However, a cumulenic resonance structure cannot put a negative charge on the carbon atom of the spacer. Thus, although the conjugated acetylene linkage can act as an effective spacer for ICT, the negative charge is highly localized on the acceptor. Therefore, it is reasonable to conclude that the excited-state dipole moment of TS-NH_2 is larger than that of DS-NH_2.

A rough estimate of the free energy changes (ΔG) associated with the exciplex is calculated using the Rehm–Weller equation [37]: ΔG (kcal/mol^{-1}) = $23.06 \times [E_{\text{ox}}(D) - E_{\text{red}}(A)] - E_{00}$, where $E_{\text{ox}}(D)$, $E_{\text{red}}(A)$, and E_{00} are the oxidation potential of the donor, the reduction potential of the acceptor and the excitation energy of the fluorophore (aniline, 296 nm), respectively. The reduction potential of naphthalene is −2.63 V [38], and the oxidation potential of aniline is 0.93 V [39]. The calculated ΔG values (−14.5 kcal/mol^{-1}) show that the formation of the exciplex is possible for SS-NH_2. The observed exciplex emission from Fig. 3 proves that a strong electronic interaction between naphthalene and aniline occurred in the excited state for SS-NH_2. It is well known that an intramolecular interaction can occur by way of a through-bond interaction (TBI) between functional groups separated by three σ-bonds [40,41] or through-space orbital overlap [42]. Upon photoexcitation, the SS-NH_2 molecule could optimize its conformation such that the donor–acceptor orbitals are antiparallel to the central C-C bond. In addition to the stabilization of a solute fluorescent state, the effect of a polar solvent can also change the electronic state and geometrical structures of a polar solute molecule in the excited state [43]. Time-resolved studies on p-N,N-dimethyl-phenyl-$(CH_2)_n$-(1-pyrenyl) and p-N,N-dimethyl-phenyl-$(CH_2)_n$-(9-anthryl) concluded that the electronic and geometrical structures of an intramolecular exciplex appear to change from a compact conformation in non-polar solvents to an extended loose conformation in polar solvents due to solute–solvent interactions [44,45]. Our work also indicates that two different exciplexes were produced for SS-NH_2 depending on the solvent polarities. The electronic structure of an exciplex $(A^{-\delta}D^{+\delta})^*(\delta \leq 1)$ of SS-NH_2 becomes more ion-pair-like ($\delta \rightarrow 1$) with increasing solvent polarity. Since it is impossible to instantiate a negative charge localized on the carbon atom of the ethylic linkage, the ICT in the excited state for SS-NH_2 almost produces an ion-pair ($\delta = 1$) complex in polar solvents.

In polar solvent, the energy gap between the exciplex and the ground states decreases but the formation rate of the exciplex increases. As increasing the nonradiative rate caused by the decrease in the energy gap and increasing the formation rate of the exciplex tend to have opposite effects on the emission, the overall effects of the solvent polarity on the fluorescence yield of the exciplex are quite complex. Therefore, the values of ratio (exciplex (ϕ_F)/LE(ϕ_F)) reach a maximum in the moderately polar solvent (EA) and decrease at higher solvent polarity.

The electron density of an amino group can be dispersed through two channels, intramolecular (ICT) and/or intermolecular interactions. If only an intramolecular channel exists inside a molecule, one can observe an ICT absorption and/or emission bands. Charge can also transfer to another molecule through an intermolecular channel. When an intermolecular interaction (hydrogen bonding and protonation) begins to compete with an intramolecular interaction, the choices among the charge-transfer pathways become subtle. Protonation can destroy the electron-donating ability of an amino group [31]; therefore, the ICT absorption and emission bands are quenched by protonation in our system (Fig. 5). Hydrogen bonding is a weak intermolecular interaction, so the charge distribution can pass through intramolecular and intermolecular channels. The electronic density of the amino group for DS-NH_2 and TS-NH_2 are reduced by hydrogen-bond formation with CF_3CH_2OH molecules in the ground-state which results in a blue-shift in the absorption maxima [30]. However, the basicity of the amino group is reduced after photoexcitation. The influence of the hydrogen-bond effect is counteracted in the excited state and only the intramolecular channel becomes predominant in charge redistribution. Therefore, the emission maxima of the ICT emission band for DS-NH_2 and TS-NH_2 were dominated by the solvent polarity. Since the polarity of CF_3CH_2OH is higher than that of CH_2Cl_2, the emission maxima display a red-shift with increasing solvent polarity. This phenomenon was named as an excited-state de-hydrogen bonding (ESDHB) process [46].

Influence of intermolecular hydrogen bonding to an intramolecular exciplex emission has been explored by many groups [47–49]. A hydrogen-bonded complex between a pretwisted pyrrolidino group and water molecules was used to explain the anomalous fluorescence of 4-pyrrolidino pyridine [47]. The exciplex fluorescence for α-helical peptide was not observed in protic solvents because the conformation and photoinduced electron transfer rate was changed by the formation of intermolecular hydrogen bonding [48]. The formation of intramolecular exciplex for 4-phenyl-1-N, N-dimethylaminobutane in THF is sensitive to the addition of alcohol [49]. The hydrogen-bonding complex formed between the amino group and the alcohol molecule decreases the electron-donating ability of amino nitrogen and suppresses the formation of the intramolecular exciplex.

The formation of the exciplex for SS-NH_2 needs the amino group and naphthalene optimize its conformation to allow a donor–acceptor electronic interaction occurred in the excited state. The intermolecular hydrogen-bond between the amino group and CF_3CH_2OH molecules blocks the reorientation of the amino group from adopting an antiperiplanar arrangement and stops the intramolecular channel. Therefore, no exciplex emission was recorded for SS-NH_2 in Fig. 6. Hydrogen bonding plays a strong role regarding the fluorescence quantum yield (ϕ_F). The ϕ_F value of TS-NH_2 decreases noticeably in methanol as compared to the corresponding value in CH_3CN. Methanol and CH_3CN are of comparable polarity but only methanol participates in the formation of hydrogen bonds with the solute molecules. Reduction in the ϕ_F values in the protic solvents for TS-NH_2 may therefore be related to a specific solute–solvent interaction [50,51].

It is important for biochemists to explore various ways in which to study a biochemical reaction regarding different biological molecules with high sensitivities in the context of qualitative and quantitative analyses. Fluorescence is the most sensitive and easily available method for studying intermolecular interactions. A good fluorescent biosensor should possess a high fluorescence quantum yield and display obvious spectral change for reflecting the microenvironment [52]. Moreover, a good fluorescent biosensor should possess little or no fluorescence in an aqueous solution; it should become a highly fluorescent species when incorporated with biological molecules. The photophysics of TS-NH_2 show it to be a good candidate regarding the design of a new fluorescent probe.

5. Conclusion

The double bond and triple bond spacers provide a more efficient ICT pathway than a flexible saturated bond. Therefore, an ICT absorption band was observed for DS-NH_2 and TS-NH_2. Although a flexible saturated bond is not enough to record an ICT absorption band, an intramolecular exciplex emission was observed for SS-NH_2. Two different exciplexes were observed for SS-NH_2 depending on the solvent polarity. The electronic structure of the exciplex of SS-NH_2 would become more ion-pair-like by increasing the solvent polarity.

The ICT absorption and emission bands were quenched by protonation in our system. An ESDHB mechanism was observed for DS-NH_2 and TS-NH_2 under the influence of CF_3CH_2OH molecules. The intermolecular hydrogen-bond between the amino group and CF_3CH_2OH molecules for SS-NH_2 block the reorientation of the amino group in the excited state and prevent the formation of an exciplex state. Therefore, no exciplex emission was recorded for SS-NH_2 in the mixed (CH_2Cl_2:CF_3CH_2OH) solvents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.12.005.

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