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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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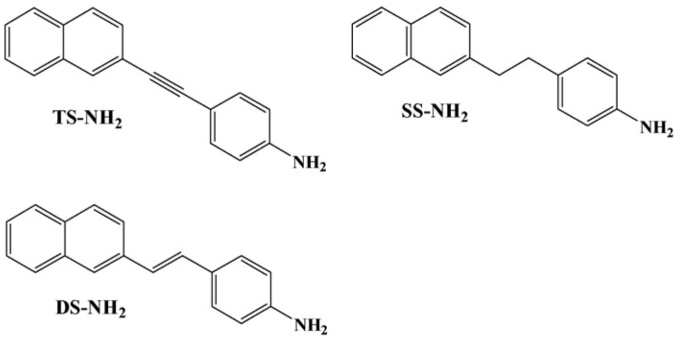

Scheme 1. The structure of compounds TS-NH$_2$, SS-NH$_2$, and DS-NH$_2$.

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$_2$.

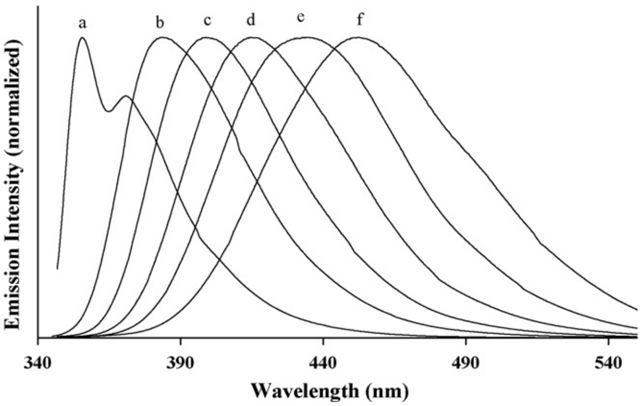

Fig. 2. The emission spectra of compound TS-NH$_2$ in different solvents. (EXC = 335 nm): (a) cyclohexane (CHX), (b) CHX90EA10 (EA: ethyl acetate), (c) CHX60EA40, (d) EA, (e) EA80ACN20, and (f) CH$_3$CN (ACN).

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

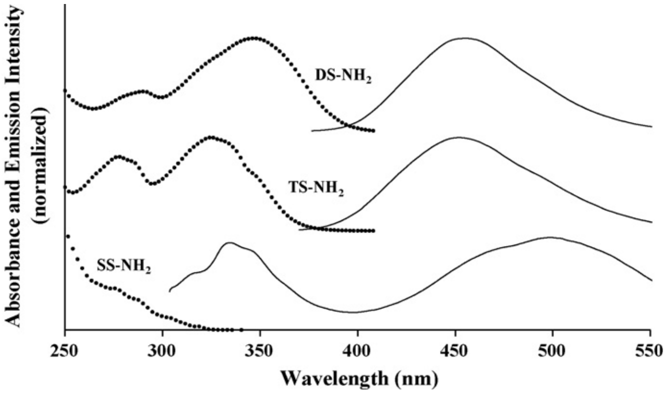

Fig. 1. The absorption and emission spectra of SS-NH$_2$ (EXC = 290 nm), DS-NH$_2$ (EXC = 350 nm), and TS-NH2 (EXC = 335 nm) in CH$_3$CN (dot line: absorption, black line: emission).

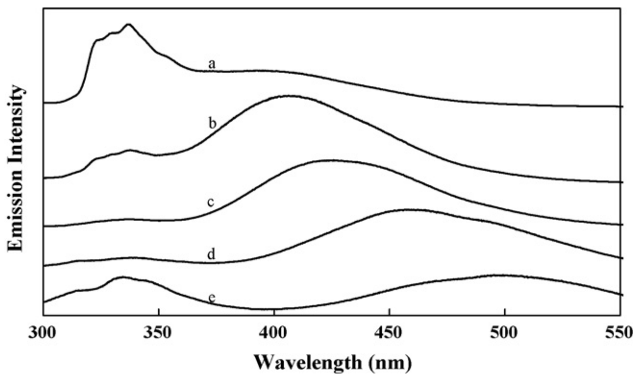

Fig. 3. The emission spectra of compound SS-NH$_2$ in different solvents (EXC = 290 nm): (a) CHX90EA10, (b) CHX60EA40, (c) EA, (d) EA80ACN20, and (e) CH$_3$CN.