

Intramolecular Charge Transfer with 1-Naphthanilides and 2-Naphthanilides

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A series of 1-naphthanilides (**1**) and 2-naphthanilides (**2**) with varied substituents at the *para*- or *meta*-position of anilino phenyl ring were prepared and their absorption and fluorescence spectra in a nonpolar solvent cyclohexane were investigated. An abnormal long wavelength emission assigned to the charge transfer (CT) state was found for all of the prepared naphthanilides in cyclohexane. A linear free energy correlation between the CT emission energies and the Hammett constants of the substituent was found within series **1** and **2**. The value of the linear slope with **1** (0.42 eV) was higher than that with **2** (0.32 eV) being close to that of the substituted benzanilides **3** (0.31 eV). The higher slope value suggested higher charge separation extent in the CT state of **1** than that of **2**. It was found that the corresponding linear slope of anilino-substituted benzanilides remained unchanged when *para*-, *meta*-, *ortho*-, or *ortho*, *ortho*-methyls were introduced into the anilino moiety, which ruled out the possible contribution of the difference in the steric effect and the electron accepting ability of the naphthoyl acceptor in **1** and **2**. Compared with the early reported *N*-substituted-benzoyl-aminonaphthalene derivatives **4** and **5**, it was considered that 1-naphthoyl enhanced the charge transfer in **1** and the proximity of its 1L_a and 1L_b states was suggested to be responsible. It was shown that 1- and/or 2-substituted naphthalene cores acting as either electron acceptor (naphthoyl) or electron donor (aminonaphthalene) were different in not only electron accepting (donating) ability but also shaping the charge transfer pathway.

Keywords intramolecular charge transfer, naphthanilide, substituent effect

Introduction

In recent years, the photophysical properties of organic molecules containing the unit of aminonaphthalene (AN) have been studied by numerous researchers¹⁻⁸ because of different radiationless internal conversion (IC) process in them. A remarkable radiationless IC process was detected in 1-aminonaphthalene (1-AN) derivatives but not in 2-aminonaphthalene (2-AN), which is probably attributed to the different energy gap between the two lowest singlet excited states $S_1(^1L_b)$ and $S_2(^1L_a)$, labeled as $\Delta E(S_1, S_2)$, in the two kinds of molecules (larger in 1-AN than in 2-AN). The IC process is especially efficient in nonpolar solvent, and along with the polarity of the solvent increasing, the efficiency of the IC reaction is decreased. The occurrence of the IC phenomenon and its polarity dependence have been attributed to the vibronic coupling of the two lowest singlet excited states $S_1(^1L_b)$ and $S_2(^1L_a)$, in which S_1 is the emissive state involving intramolecular charge transfer.

Recently, we⁹ reported the dual fluorescence of

N-(substituted-benzoyl)aminonaphthalenes (**4** and **5**, Scheme 1) in cyclohexane using the charge transfer in benzanilides as a probe reaction, in which the 1-AN or 2-AN was considered as electron donors while the benzoyl moiety as the electron acceptor. It showed that the charge transfer in **4** and **5** was not the same. 1-AN and 2-AN as electron donors were different in not only electron donating ability but also shaping the charge transfer pathway as well.⁹ The enhanced charge transfer in **4** versus **5** was ascribed to the proximity of the 1L_a and 1L_b states in 1-AN that allows for a better vibronic coupling which is important for the charge transfer reaction.

These results encourage us to extend the research to the possible charge transfer in 1-naphthanilides **1** and 2-naphthanilides **2** (Scheme 1) with *para*- or *meta*-substituent at the anilino phenyl ring, in which the naphthoyl was considered as electron acceptor while the amido aniline as electron donor. The purpose is to probe the difference in the electron accepting ability of 1- and 2-naphthoyls and their ability in shaping charge transfer.

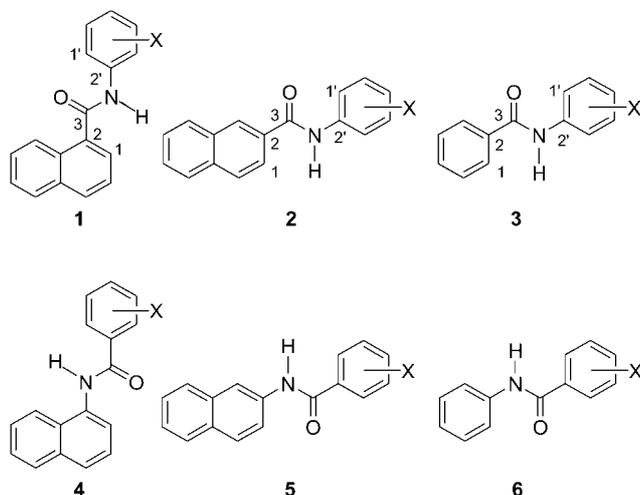
Naphthanilides can be considered as a kind of ben-

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Scheme 1 Molecular structure of **1**–**6**. Substituents X of **1** and **2** are *p*-OC₂H₅ (**a**), *p*-CH₃ (**b**), H (**c**), *p*-F (**d**), *p*-Cl (**e**), *p*-Br (**f**), *m*-Br (**g**), *p*-COCH₃ (**h**), *m*-NO₂ (**i**), and *p*-NO₂ (**j**), respectively. The numbers shown in the structures were only used to define the dihedral angles



zanilide derivatives. Intramolecular charge transfer might be expected and actually indeed takes place in these molecules characterized by the dual fluorescence emission.^{10–12} In this paper, we report the synthesis and the optical spectra of **1** and **2**. We will show that charge transfer occurred with **1** and **2** in cyclohexane. Furthermore, 1- and 2-naphthoyl moieties differ in their electron accepting ability and their ability of defining the charge transfer pathway in **1** and **2**.

Experimental

Methods

Structure of **1** and **2** was confirmed by ¹H NMR (Varian Unity⁺, 500 MHz, DMSO-*d*₆, TMS), IR (Nicolet Avatar FT-IR 360) and ESI-MS (Bruker Dalton Esquire 3000 plus and Finnigan Mat-LCQ, ESI direct injection) data. Corrected fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrometer using an excitation wavelength of 300 nm for **1** and **2** by a Xenon lamp at 150 W. The slits for excitation and emission monochromators were 5 and 10 nm, respectively. A scan rate of 240 nm·min⁻¹ was chosen. Fluorescence quantum yields were measured using quinine sulfate (0.546 in 0.5 mol·L⁻¹ H₂SO₄) as a standard.¹³ The absorption spectra were taken on a Varian Cary 300 UV-Vis spectrophotometer using a 1-cm quartz cell. All spectra were measured at a sample concentration of *ca.* 10⁻⁵ mol·L⁻¹ at room temperature of *ca.* 298 K. The ground-state geometrical structures were optimized by a semi-empirical AM1 method using MOPAC programs (version 97.0) in Alchemy 2000 software package.¹⁴ Solvents used for fluorescence and absorption spectra measurements were purified just before use and checked to have no fluorescent impurity at the employed excitation wavelength.

Materials

1 and **2** were synthesized from the reactions of substituted-anilines with 1- or 2-naphthoyl chloride in the presence of anhydrous Na₂CO₃ in diethyl ether.¹⁵ The naphthoyl chlorides were *in situ* prepared from the corresponding naphthoic acids and SOCl₂. All products were purified by repeated recrystallizations from acetone.

4'-Ethoxy-1-naphthanilide (1a): ¹H NMR δ: 1.33 (t, *J*=6.5 Hz, 3H), 4.00–4.04 (m, 2H), 6.94 (d, *J*=9.0 Hz, 2H), 7.55–7.63 (m, 3H), 7.23 (t, *J*=8.0 Hz, 3H), 7.98–8.04 (m, 1H), 8.07 (d, *J*=8.0 Hz, 1H), 8.16–8.22 (m, 1H), 10.42 (s, 1H); IR (KBr) ν: 3240, 1647 cm⁻¹; ESI-MS for C₁₉H₁₇NO₂ calcd: 291.3 (M⁺), found 292.1 (M+H⁺), 314.0 (M+Na⁺).

4'-Methyl-1-naphthanilide (1b): ¹H NMR δ: 2.29 (s, 3H), 7.18 (d, *J*=8.5 Hz, 2H), 7.56–7.64 (m, 3H), 7.66–7.76 (m, 3H), 7.99–8.04 (m, 1H), 8.07 (d, *J*=8.5 Hz, 1H), 8.15–8.20 (m, 1H), 10.48 (s, 1H); IR (KBr) ν: 3266, 1652 cm⁻¹; ESI-MS for C₁₈H₁₅NO calcd: 261.3 (M⁺), found 262.1 (M+H⁺), 284.0 (M+Na⁺).

1-Naphthanilide (1c): ¹H NMR δ: 7.12 (t, *J*=7.0 Hz, 1H), 7.37 (t, *J*=7.0 Hz, 2H), 7.56–7.64 (m, 3H), 7.75 (d, *J*=7.0 Hz, 1H), 7.81 (d, *J*=7.5 Hz, 2H), 8.00–8.06 (m, 1H), 8.08 (d, *J*=8.0 Hz, 1H), 8.18 (d, *J*=6.5 Hz, 1H), 10.57 (s, 1H); IR (KBr) ν: 3288, 1651 cm⁻¹; ESI-MS for C₁₇H₁₃NO calcd: 247.3 (M⁺), found 248.1 (M+H⁺), 270.0 (M+Na⁺).

4'-Fluoro-1-naphthanilide (1d): ¹H NMR δ: 7.23 (t, *J*=8.0 Hz, 2H), 7.56–7.64 (m, 3H), 7.76 (d, *J*=7.0 Hz, 1H), 7.80–7.87 (m, 2H), 7.99–8.05 (m, 1H), 8.08 (d, *J*=8.0 Hz, 1H), 8.18 (d, *J*=6.0 Hz, 1H), 10.63 (s, 1H); IR (KBr) ν: 3282, 1649 cm⁻¹; ESI-MS for C₁₇H₁₂FNO calcd: 265.3 (M⁺), found 266.0 (M+H⁺), 287.9 (M+Na⁺).

4'-Chloro-1-naphthanilide (1e): ¹H NMR δ: 7.44 (dd, *J*=8.5, 1.5 Hz, 2H), 7.56–7.65 (m, 3H), 7.76 (d, *J*=7.5 Hz, 1H), 7.85 (d, *J*=8.5 Hz, 2H), 8.00–8.05 (m, 1H), 8.09 (d, *J*=8.5 Hz, 1H), 8.14–8.20 (m, 1H), 10.71 (s, 1H); IR (KBr) ν: 3225, 1652 cm⁻¹; ESI-MS for C₁₇H₁₂ClNO calcd: 281.7 (M⁺), found 282.0 (M+H⁺), 303.9 (M+Na⁺).

4'-Bromo-1-naphthanilide (1f): ¹H NMR δ: 7.57 (d, *J*=7.5 Hz, 2H), 7.58–7.64 (m, 3H), 7.76 (d, *J*=7.0 Hz, 1H), 7.80 (d, *J*=8.5 Hz, 2H), 8.00–8.05 (m, 1H), 8.09 (d, *J*=7.5 Hz, 1H), 8.14–8.19 (m, 1H), 10.71 (s, 1H); IR (KBr) ν: 3221, 1651 cm⁻¹; ESI-MS for C₁₇H₁₂BrNO calcd: 325.0 (M⁺), found 325.9 (M+H⁺), 347.9 (M+Na⁺).

3'-Bromo-1-naphthanilide (1g): ¹H NMR δ: 7.29–7.39 (m, 2H), 7.57–7.67 (m, 3H), 7.73 (d, *J*=7.0 Hz, 1H), 7.77 (d, *J*=7.0 Hz, 1H), 8.00–8.06 (m, 1H), 8.10 (d, *J*=8.0 Hz, 1H), 8.15–8.22 (m, 2H), 10.75 (s, 1H); IR (KBr) ν: 3275, 1650 cm⁻¹; ESI-MS for C₁₇H₁₂BrNO calcd: 325.0 (M⁺), found 325.9 (M+H⁺), 347.9 (M+Na⁺).

4'-Acetyl-1-naphthanilide (1h): ¹H NMR δ: 2.57 (s, 3H), 7.56–7.70 (m, 3H), 7.78 (d, *J*=6.5 Hz, 1H), 7.96

(d, $J=8.5$ Hz, 2H), 7.98—8.08 (m, 3H), 8.11 (d, $J=8.0$ Hz, 1H), 8.18 (d, $J=8.0$ Hz, 1H), 10.92 (s, 1H); IR (KBr) ν : 3221, 1675 cm^{-1} ; ESI-MS for $\text{C}_{19}\text{H}_{15}\text{NO}_2$ calcd: 289.3 (M^+), found 290.1 ($\text{M}+\text{H}^+$), 312.0 ($\text{M}+\text{Na}^+$).

3'-Nitro-1-naphthanilide (1i): ^1H NMR δ : 7.58—7.72 (m, 4H), 7.83 (d, $J=7.0$ Hz, 1H), 8.00 (d, $J=8.0$ Hz, 1H), 8.02—8.08 (m, 1H), 8.13 (t, $J=7.0$ Hz, 2H), 8.19—8.26 (m, 1H), 8.89 (s, 1H), 11.07 (s, 1H); IR (KBr) ν : 3226, 1651 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$ calcd: 292.3 (M^+), found 293.0 ($\text{M}+\text{H}^+$), 314.9 ($\text{M}+\text{Na}^+$).

4'-Nitro-1-naphthanilide (1j): ^1H NMR δ : 7.58—7.68 (m, 3H), 7.83 (d, $J=7.0$ Hz, 1H), 8.02—8.10 (m, 3H), 8.13 (d, $J=8.0$ Hz, 1H), 8.16—8.22 (m, 1H), 8.31 (d, $J=9.0$ Hz, 2H), 11.19 (s, 1H); IR (KBr) ν : 3230, 1658 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$ calcd: 292.3 (M^+), found 293.0 ($\text{M}+\text{H}^+$), 314.9 ($\text{M}+\text{Na}^+$).

4'-Ethoxy-2-naphthanilide (2a): ^1H NMR δ : 1.33 (t, $J=6.5$ Hz, 3H), 4.00—4.04 (m, 2H), 6.94 (d, $J=9.0$ Hz, 2H), 7.60—7.67 (m, 2H), 7.72 (d, $J=8.5$ Hz, 2H), 7.99—8.07 (m, 3H), 8.08 (d, $J=7.5$ Hz, 1H), 8.56 (s, 1H), 10.30 (s, 1H); IR (KBr) ν : 3344, 1652 cm^{-1} ; ESI-MS for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ calcd: 291.3 (M^+), found 292.0 ($\text{M}+\text{H}^+$).

4'-Methyl-2-naphthanilide (2b): ^1H NMR δ : 2.30 (s, 3H), 7.18 (d, $J=8.0$ Hz, 2H), 7.60—7.67 (m, 2H), 7.71 (d, $J=8.5$ Hz, 2H), 7.99—8.07 (m, 3H), 8.09 (d, $J=7.5$ Hz, 1H), 8.57 (s, 1H), 10.35 (s, 1H); IR (KBr) ν : 3260, 1642 cm^{-1} ; ESI-MS for $\text{C}_{18}\text{H}_{15}\text{NO}$ calcd: 261.3 (M^+), found 262.2 ($\text{M}+\text{H}^+$).

2-Naphthanilide (2c): ^1H NMR δ : 7.12 (t, $J=7.5$ Hz, 1H), 7.38 (t, $J=7.5$ Hz, 2H), 7.60—7.67 (m, 2H), 7.83 (d, $J=8.0$ Hz, 2H), 8.00—8.08 (m, 3H), 8.09 (d, $J=7.5$ Hz, 1H), 8.58 (s, 1H), 10.57 (s, 1H); IR (KBr) ν : 3362, 1659 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{13}\text{NO}$ calcd: 247.3 (M^+), found 248.0 ($\text{M}+\text{H}^+$).

4'-Fluoro-2-naphthanilide (2d): ^1H NMR δ : 7.23 (t, $J=8.5$ Hz, 2H), 7.60—7.68 (m, 2H), 7.86 (dd, $J=8.5$, 5.0 Hz, 2H), 8.00—8.08 (m, 3H), 8.09 (d, $J=7.0$ Hz, 1H), 8.59 (s, 1H), 10.50 (s, 1H); IR (KBr) ν : 3378, 1656 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{FNO}$ calcd: 265.3 (M^+), found 266.0 ($\text{M}+\text{H}^+$).

4'-Chloro-2-naphthanilide (2e): ^1H NMR δ : 7.44 (d, $J=9.0$ Hz, 2H), 7.60—7.68 (m, 2H), 7.88 (d, $J=9.0$ Hz, 2H), 7.99—8.08 (m, 3H), 8.10 (d, $J=7.5$ Hz, 1H), 8.58 (s, 1H), 10.56 (s, 1H); IR (KBr) ν : 3376, 1659 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{ClNO}$ calcd: 281.7 (M^+), found 282.0 ($\text{M}+\text{H}^+$).

4'-Bromo-2-naphthanilide (2f): ^1H NMR δ : 7.57 (d, $J=8.5$ Hz, 2H), 7.60—7.69 (m, 2H), 7.82 (d, $J=9.0$ Hz, 2H), 7.99—8.08 (m, 3H), 8.10 (d, $J=7.5$ Hz, 1H), 8.58 (s, 1H), 10.55 (s, 1H); IR (KBr) ν : 3375, 1659 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{BrNO}$ calcd: 325.0 (M^+), found 325.9 ($\text{M}+\text{H}^+$).

3'-Bromo-2-naphthanilide (2g): ^1H NMR δ : 7.30—7.38 (m, 2H), 7.61—7.69 (m, 2H), 7.82 (d, $J=8.5$ Hz, 1H), 7.99—8.05 (m, 2H), 8.07 (d, $J=8.5$ Hz, 1H), 8.10

(d, $J=8.0$ Hz, 1H), 8.16 (s, 1H), 8.59 (s, 1H), 10.57 (s, 1H); IR (KBr) ν : 3266, 1647 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{BrNO}$ calcd: 325.0 (M^+), found 325.9 ($\text{M}+\text{H}^+$).

4'-Acetyl-2-naphthanilide (2h): ^1H NMR δ : 2.56 (s, 3H), 7.60—7.70 (m, 2H), 7.95—8.05 (m, 6H), 8.08 (d, $J=9.0$ Hz, 1H), 8.11 (d, $J=7.5$ Hz, 1H), 8.62 (s, 1H), 10.75 (s, 1H); IR (KBr) ν : 3369, 1673 cm^{-1} ; ESI-MS for $\text{C}_{19}\text{H}_{15}\text{NO}_2$ calcd: 289.3 (M^+), found 290.0 (M^++H^+).

3'-Nitro-2-naphthanilide (2i): ^1H NMR δ : 7.62—7.72 (m, 3H), 7.99 (d, $J=8.0$ Hz, 1H), 8.05 (t, $J=8.0$ Hz, 2H), 8.11 (t, $J=9.0$ Hz, 2H), 8.26 (d, $J=8.0$ Hz, 1H), 8.64 (s, 1H), 8.86 (s, 1H), 10.89 (s, 1H); IR (KBr) ν : 3289, 1652 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$ calcd: 292.3 (M^+), found 293.0 ($\text{M}+\text{H}^+$).

4'-Nitro-2-naphthanilide (2j): ^1H NMR δ : 7.62—7.71 (m, 2H), 8.04 (d, $J=8.5$ Hz, 2H), 8.09 (d, $J=8.5$ Hz, 2H), 8.12 (d, $J=9.0$ Hz, 2H), 8.31 (d, $J=9.0$ Hz, 2H), 8.63 (s, 1H), 11.00 (s, 1H); IR (KBr) ν : 3263, 1651 cm^{-1} ; ESI-MS for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$ calcd: 292.3 (M^+), found 293.0 ($\text{M}+\text{H}^+$).

Results and discussion

The ground state structure of 1-naphthanilides and 2-naphthanilides

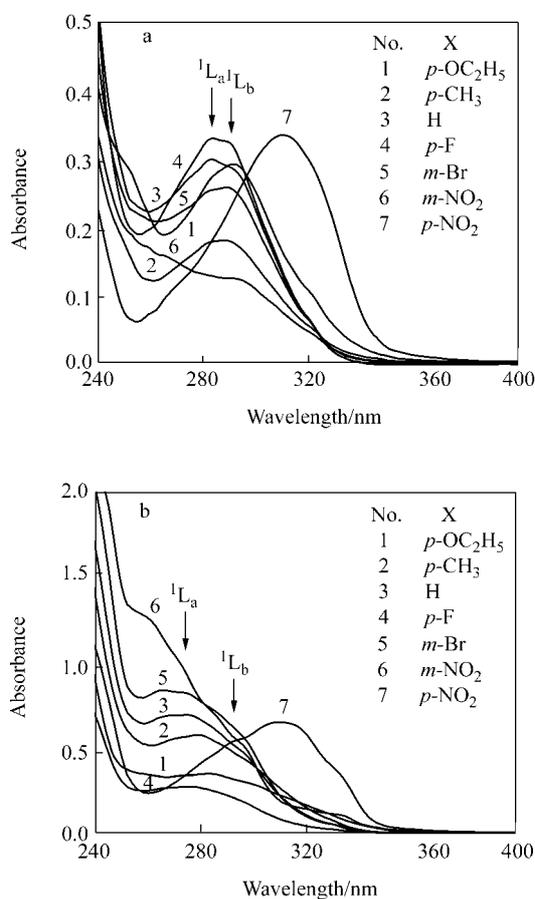
In order to avoid the possible complexity resulting from the *ortho* substituent, only *para*- or *meta*-substituted **1** and **2** were synthesized. The semi-empirical AM1 calculations indicated that **1** or **2** in the *trans*-configuration was lower in energy by 35.1 $\text{kJ}\cdot\text{mol}^{-1}$ than that in the *cis*-configuration, revealing that **1** and **2** existed preferentially in the *trans*-form as shown for benzanilides. The following calculations were therefore carried out only on the *trans*-amides. The ground-state structural parameters of all of the *trans*-naphthanilide derivatives optimized by AM1 method are compiled in Table 1. It follows from Table 1 that the aniline substitution does not result in obvious change in the ground state structures within the same series. The fact that the dihedral angle $\angle\text{C}(1)-\text{C}(2)-\text{C}(3)-\text{N}$ of **1** is much larger than that in **2** suggests the steric effects of the substitution *ortho* to the $\text{C}=\text{O}$ group and/or of the *peri*-H at C-8 on the naphthoyl moiety of **1**. The weak dependence of the ground state structures on the substitution reflected the similarity of the locally excited (LE) state structure within the same series.

The absorption spectra of **1** and **2** in cyclohexane confirmed this assumption (Figure 1 and Table 2). Figure 1 illustrates parts of the absorption spectra of **1** and **2**. Obviously, the absorption spectrum of naphthanilide was similar to naphthamide with a maximum at *ca.* 289 nm.¹⁶ Three bands can be seen in the absorption spectra of **1** and **2**. The band with a λ_{max} of 225 nm belongs to $^1\text{B}_b\leftarrow^1\text{A}$ transition, and the two main absorption bands are due to the $^1\text{L}_a\leftarrow^1\text{A}$ and $^1\text{L}_b\leftarrow^1\text{A}$ transitions, respectively.¹¹ The absorption of **1** peaked at 284 nm

Table 1 AM1 optimized ground state structural parameters of **1** and **2**

X	1			2		
	Dihedral angle/(°)		Dipole moment/D	Dihedral angle/(°)		Dipole moment/D
	$\angle C(1)-C(2)-C(3)-N^a$	$\angle C(3)-N-C(2)-C(1)^a$		$\angle C(1)-C(2)-C(3)-N^a$	$\angle C(3)-N-C(2)-C(1)^a$	
a	59.3	12.5	4.29	43.3	11.0	4.38
b	59.3	7.6	3.18	43.6	6.1	3.36
c	59.7	8.7	3.33	44.1	5.9	3.54
d	59.6	9.7	4.46	43.6	7.4	4.84
e	59.9	7.2	4.29	43.6	5.7	4.65
f	59.7	5.9	4.46	43.8	4.9	4.85
g	59.6	8.2	3.06	43.6	6.4	3.49
h	59.4	4.6	4.18	43.5	3.4	4.72
i	58.8	7.5	5.22	43.2	3.9	5.79
j	59.6	3.9	8.52	42.9	2.7	9.08

^a The atom numbering was shown in Scheme 1.

**Figure 1** Absorption spectra of **1** (a) and **2** (b) in cyclohexane.

(${}^1L_a \leftarrow {}^1A$) was found to be well mixed with that of the ${}^1L_b \leftarrow {}^1A$ transition, appearing as a shoulder at around 289 nm. Meanwhile, it was found that the broad absorption of **2** at *ca.* 290 nm originating from the ${}^1L_b \leftarrow {}^1A$ transition was obviously separated from the ${}^1L_a \leftarrow {}^1A$ absorption lied at *ca.* 270 nm. The position and shape of the absorption spectra within **1** or **2** series, respectively, were hardly changed when the substituent was varied

from electron-donating group to electron-withdrawing group, see Figure 1 and Table 2. The *p*-nitro derivatives, as exception, had absorption tails extending to longer wavelength, probably indicating the occurrence of the ground-state charge transfer. These comparable absorption spectra indicated the same ground structure within the series compound of **1** and **2**.

With increasing electron-withdrawing ability of the substituent at the amido aniline phenyl ring in **1** and **2**, the 1H NMR chemical shift of the amido NH proton experienced a continuous downfield shift (Figure 2), which was indicated by nice linear dependence of the chemical shift against Hammett constants σ_x ¹⁷ with slopes of 0.70 for **1** and 0.63 for **2**, respectively. This means that a monotonous decrease in the electron density at the amido NH nitrogen occurs with increasing electron-withdrawing ability of the substituent. The slopes of **1** and **2** are similar to the slope of *p*-dimethylaminobenzanilides (0.66),¹⁸ which was re-

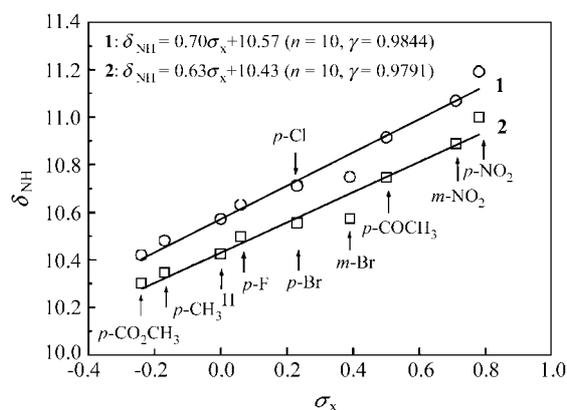
**Figure 2** Linear dependence of the 1H NMR chemical shift of the amido NH proton against the Hammett constant of the substituent at the amido aniline phenyl ring of **1** and **2**, respectively. The 1H NMR data were acquired in $DMSO-d_6$ using tetramethylsilane (TMS) as an internal standard.

Table 2 Spectroscopic data of **1** and **2** in cyclohexane

X	1				2			
	$\lambda_{\text{abs}}/\text{nm}$	$\varepsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$	$\lambda_{\text{flu}}/\text{nm}$	Quantum yield (Φ)	$\lambda_{\text{abs}}/\text{nm}$	$\varepsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$	$\lambda_{\text{flu}}/\text{nm}$	Quantum yield (Φ)
a	291.0	9733	— ^a	— ^a	292.0	6633	— ^a	— ^a
b	288.0	12133	555.0	0.0003	289.0	14000	520.0	0.0008
c	288.0	10133	535.0	0.0005	288.0	16267	500.0	0.0007
d	287.0	10600	540.0	0.0005	289.0	9200	504.0	0.0010
e	289.0	14133	525.0	0.0005	288.0	6400	495.0	0.0013
f	289.0	14867	518.0	0.0006	289.0	5033	492.0	0.0007
g	289.0	11067	502.0	0.0004	288.0	9067	483.0	0.0010
h	291.0	9100	494.0	— ^b	286.0	9433	473.0	— ^b
i	287.0	6267	— ^b	— ^b	— ^a	— ^a	— ^b	— ^b
j	311.0	9233	— ^b	— ^b	312.0	7367	— ^b	— ^b

^a Difficult to read accurately. ^b Too weak to estimate accurately.

ported recently. The similarity of the slope of **1**, **2** and *p*-dimethylaminobenzanilides could result from the similar ground state structure.

Fluorescence spectroscopy of 1-naphthanilides and 2-naphthanilides

The fluorescence spectra of **1** and **2** in cyclohexane were shown in Figure 3, where it was seen that **1** and **2** derivatives exhibited CT fluorescence. The long-wavelength fluorescence was found to shift to the red with increasing electron-donating ability of the substituent at the aniline moiety, as observed with **3**. The long wavelength emissions of **1** and **2** were assigned to the intramolecular charge transfer (ICT) state with naphthoyl and substituted aniline being electron acceptor and donor, respectively, as similarly done with aniline-substituted benzanilides **3**.¹⁹ The CT nature was further supported by the substantial red shift of the long wavelength emission with increasing solvent polarity (data not shown).

Linear free energy correlation between the CT emission energies and the Hammett constants

Benzanilides have been investigated since 1970's because of their dual fluorescence in nonpolar solvents.¹⁸⁻²⁹ The weak short-wavelength emission was attributed to the locally excited (LE) state, whereas the long-wavelength emission with a large Stokes shift has been assigned to an imido tautomer, a twisted intramolecular charge transfer (TICT) state, or the overlap of the two. Based on systemic studies of the substituted benzanilides (**3** and **6**, Scheme 1),^{19,29} it has been revealed that the long-wavelength emission of benzanilide was strongly dependent on the electron donating or accepting capacity of the substituent at the anilino or benzoyl moiety. The CT emission energies varied linearly with the Hammett constants of the substituents at the anilino or benzoyl moiety. This result provided direct spectroscopic evidence for the charge transfer nature of the long-wavelength emission of **3** and **6**. It was shown

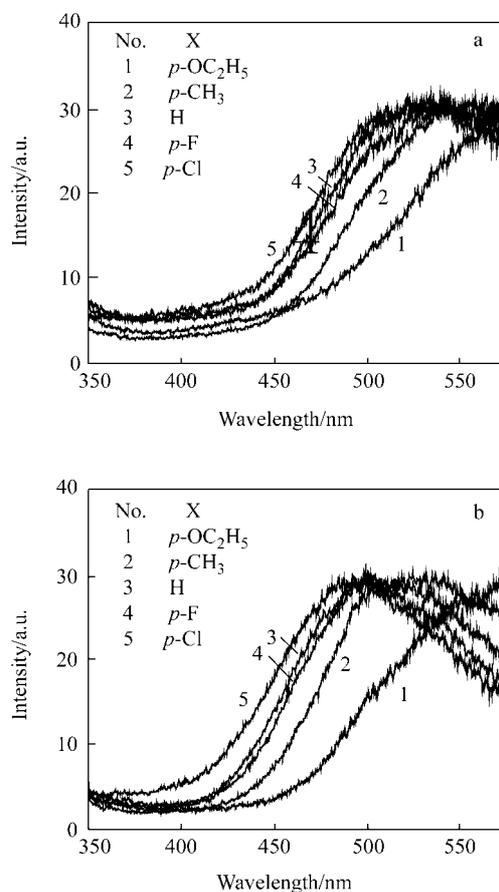


Figure 3 Normalized fluorescence spectra of **1** (a) and **2** (b) in cyclohexane.

that within **3** or **6** the CT emission energies varied linearly with the Hammett constants of the substituents in terms of Eq. (1).^{19,29}

$$h\nu_{\text{max}}(\text{CT}) = -2.303RT\rho\sigma + E_{0,0} - \delta E_{\text{rep}} + C \quad (1)$$

In Eq. (1), $E_{0,0}$ is the (0,0)-transition energy, δE_{rep} the repulsion energy of the Franck-Condon ground state reached after CT emission, σ the Hammett constant of

the substituent, ρ the reaction constant defined in the classic Hammett equation,³⁰ R and T are the gas constant and absolute temperature and C is a constant. A negative or positive ρ indicates that electron-donating or electron-withdrawing substituent enhances the involved reaction. It is obvious that a linear relationship between $h\nu_{\max}(\text{CT})$ and σ will be held when both $E_{0,0}$ and δE_{rep} or their difference remains constant within the series. The linear slope indicates the charge transfer extent in the CT state while the intercept indexes the electron-withdrawing (electron donating) ability of the unsubstituted benzoyl (anilino) moiety.

From the data obtained by quantum mechanical calculation and absorption spectra, it can be concluded that weak dependence on the substitution exists in series compounds of **1** and **2** in the ground state. From this result, it can be assumed that both $E_{0,0}$ and δE_{rep} remain constant within **1** and **2**, respectively, which means that Eq. 1 would be held for **1** and **2** for clarifying the charge transfer character as that has been done with **3**, **4**, **5** and **6**. Therefore, it is possible to employ the CT reaction in benzanilides to probe the charge transfer character of **1** and **2**.

A linear free energy correlation between the CT emission energies and the Hammett constants¹⁷ of the substituent was found with **1** and **2** series (Figure 4). Considering **1** and **2** series respectively, the value of the linear slope with **1** (0.42 eV, $\gamma=0.9778$, $n=7$) was found to be higher than that with **2** (0.32 eV, $\gamma=0.9771$, $n=7$), and the latter was close to that of **3** (0.31 eV, $\gamma=0.9651$, $n=6$), which indicated that the charge transfer in **1** and **2** were different with the latter being similar to that of **3**. Based on Eq. 1, the ρ values were calculated as -7.36 for **1**, -5.61 for **2** and -5.43 for **3**, which indicated a higher charge separation extent in the CT state of **1** than that of **2** by the higher slope value. This difference in the linear slope for **1** and **2** could result in principle from the differences in the electron-accepting abilities of 1-naphthoic acid and 2-naphthoic acid as electron acceptor. The lower intercept in the linear correlation of **1** (Figure 4) is actually indicative of higher electron accepting ability of 1-naphthoic acid, which is in agreement with the known data of lower $\text{p}K_{\text{a}}$ value of 1-naphthoic acid ($\text{p}K_{\text{a}}=3.70$) than that of 2-naphthoic acid ($\text{p}K_{\text{a}}=4.17$).³¹

The charge separation extent in the CT state of **1** and **2** was further evaluated by correlating the CT emission energies with their oxidation potentials.³² The linear dependence was also found with a slope of 0.79 for **1** ($\gamma=0.9284$, $n=5$), and 0.66 for **2** ($\gamma=0.9211$, $n=5$), close to $+1$ that is expected for the complete charge separation as observed with the exciplex (Eq. 2).³³

$$h\nu_{\text{CT}} = E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} - \delta E_{\text{rep}} + 0.15 \quad (2)$$

Comparing the slope of **1** (0.79) and **2** (0.66) obtained above with the slope of **3** (0.66, $\gamma=0.9874$, $n=5$)

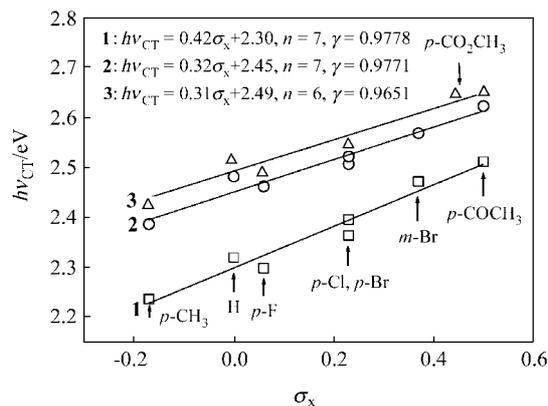


Figure 4 Linear correlation between the CT emission energies of **1**, **2** and **3** in cyclohexane and the Hammett substituent constant. The CT emission energy data of **3** were taken from Ref. 19.

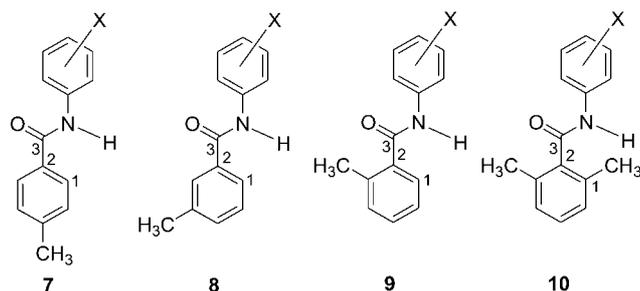
we have reported early,¹⁹ it showed that the charge separation extent of **2** and **3** has some similarity. The higher extent of charge separation in the CT state was shown by a higher value of linear slope for **1**, suggesting that 1-naphthoyl enhance the charge transfer reaction in **1**.

The observation either from correlation between $h\nu_{\text{CT}}$ and the Hammett constants of the substituent or from correlation between $h\nu_{\text{CT}}$ and their oxidation potentials showed the same result. The charge transfer in **2** was similar to that in **3**, pointed to the similarity of 2-naphthoyl as electron acceptor to benzoyl.

To elucidate the difference of steric effect and electron accepting ability between **1** and **2**, four series model compounds **7**, **8**, **9** and **10** (Scheme 2) were prepared,³⁴ in which **7** and **8** have the different electron accepting ability of the benzoyl acceptor and **9** and **10** do the steric hindrance that could exist between **1** and **2**. The steric effect in the four series was shown by the dihedral angle $\angle\text{C}(1)\text{-C}(2)\text{-C}(3)\text{-N}$ obtained from AM1 calculation, which increased from an average of 43.6° for **7**, 43.5° for **8**, 60.1° for **9**, to 77.2° for **10**. Investigation on the properties of charge transfer reactions showed similar linear slope (0.24 eV) for the correlation between $h\nu_{\text{CT}}$ and the Hammett constants for all of the four series derivatives, which suggested that neither difference in the electron accepting ability of electron acceptor nor the difference in the steric effect between **1** and **2** results in obvious difference in the linear slope for the correlation between the CT emission energy and Hammett substituent constant. Therefore, it was made clear that the difference in the linear slope for **1** and **2** was not due to the difference in the electron accepting ability of naphthoyl acceptor and the steric effect in **1**, which means that 1-naphthoyl and 2-naphthoyl, as electron acceptor, differ not only in their electron accepting abilities.

According to the theory depicted by Platt,³⁵ the two lowest $^1(\pi, \pi^*)$ states for the parent molecule naphthalene are $S_1(^1L_{\text{b}})$ and $S_2(^1L_{\text{a}})$. The lowest singlet excited state S_1 is of $^1L_{\text{b}}$ character and its transition dipole mo-

Scheme 2 Molecular structures of the methyl substituted benzanilides. The numbers shown in the structures were only used to define the dihedral angles, $\angle C(1)-C(2)-C(3)-N$



ment is oriented along the long molecular axis, whereas the S_2 state is of 1L_a nature and is short axis polarized. Hence, the electronic distributions in the two electronic states are quite different. With 1-naphthanilides, the 1-substituted derivatives of naphthalene stabilize the $S_2(^1L_a)$ state and decrease the $\Delta E(S_1, S_2)$ energy gap, which will strongly enhance the vibronic coupling between the 1L_a and 1L_b states. Contrast with 1-naphthanilides, 2-substituted derivatives of naphthalene stabilize the lower long axis polarized $S_1(^1L_b)$ state, leading to a relatively large value for $\Delta E(S_1, S_2)$.^{2-6,9} These different substituent effects can be seen from the absorption spectra of **1**, **2** and **4**, **5**.

From the absorption spectra, it can be observed that the 1L_a and 1L_b states exist with proximity in **1** and **4** compound series, whereas the 1L_a and 1L_b states of **2** and **5** have been obviously separated from each other. Comparing the charge transfer reaction properties of **1** and **2** with the early reported **4** and **5**,⁹ it is easy to draw the conclusion that 1-naphthoyl and 1-aminonaphthalene could induce the enhanced charge transfer compared to 2-naphthoyl and 2-aminonaphthalene. Based on the above results, it is assumed that the enhanced charge transfer observed for **1** and **4** than for **2** over **5** resulted from an enhanced vibronic coupling of the 1L_a and 1L_b states occurring in the 1-substituted parent naphthalene molecule. This finding showed that the 1- and/or 2-substituted naphthalene nuclei acting as either electron acceptor (naphthoyl) or electron donor (aminonaphthalene) were different in shaping the charge transfer pathway.

Conclusion

Using benzanilide like charge transfer as a probe reaction, the spectral character of **1** and **2** series compounds has been systematically investigated with substituents at the *para*- or *meta*-position of aniline phenyl ring. All of the derivatives were found to emit charge transfer emission at around 500 nm in cyclohexane, while the absorption showed very weak dependence on the substitution. The long-wavelength fluorescence was found to shift to the red with increasing electron donating ability of the substituent at the aniline moiety. The charge separation extent in the CT state of **1** and **2** was

evaluated by correlating the CT emission energies with Hammett constants of the substituent and their oxidation potential and better linear relationships were obtained. A higher slope was obtained for **1** than for **2**, clearly pointing to a higher charge separation extent in the CT state of **1**. With the possible contribution to the electron accepting ability of 1-naphthoyl and 2-naphthoyl and to the steric effect due to the substitution *ortho* to the C=O group and/or of the *peri*-H at C-8 in **1** being ruled out, it could be considered that the enhanced charge transfer observed for **1** compared to **2** resulted from an enhanced vibronic coupling of the 1L_a and 1L_b states occurring in the 1-substituted naphthoic acid. Combined with the result from **4** and **5** that reported early, it was shown that 1- and/or 2-substituted naphthalene nuclei acting as either electron acceptor (naphthoyl) or electron donor (aminonaphthalene) were different in not only electron accepting (donating) ability but also shaping the charge transfer pathway.

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