Intramolecular charge transfer with *N*-benzoylaminonaphthalenes. 1-Aminonaphthalene *versus* 2-aminonaphthalene as electron donors

Xuan Zhang,[a] **Chun-Hua Liu,**[a] **Li-Hong Liu,**[a] **Fang-Ying Wu,**[a,b] **Lin Guo,**[a] **Xiang-Ying Sun,**[a,c] **Chao-Jie Wang**[d] **and Yun-Bao Jiang ***[a]

[a] *Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China*

[b] *Department of Chemistry, Nanchang University, Nanchang 310047, China*

[c] *Department of Environmental Science and Engineering, Huaqiao University, Quanzhou 362011, China*

[d] *Department of Chemistry and the State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China*

N-(substituted-benzoyl)-1-aminonaphthalenes and *N*-(substituted-benzoyl)-2-aminonaphthalenes (1-NBAs and 2-NBAs) with varied substituents at the *para*- or *meta*-position of benzoyl phenyl ring were prepared to probe the difference between 1-aminonaphthalene (1-AN) and 2-aminonaphthalene (2-AN) as electron donors, using benzanilide-like charge transfer as a probe reaction. An abnormal long-wavelength emission was found for all of the prepared aminonaphthalene derivatives in cyclohexane and was assigned to the CT state by the observation of a substantial red shift with increasing solvent polarity or with increasing electron-withdrawing ability of the substituent. The CT emission energies were found to follow a linear relationship with the Hammett constant of the substituent and the value of the linear slope for 1-NBAs (-0.45 eV) was higher than that of 2-NBAs (-0.35 eV), the latter being close to that of the aniline derivatives (BAs, -0.345 eV). This pointed to a higher extent of charge separation in the CT state of 1-NBAs in which a full charge separation was established by the reduction potential dependence of the CT emission energy with a linear slope of -1.00. The possible contribution of the difference in the steric effect and the electron donating ability of the donors in 1-NBAs and 2-NBAs was ruled out by the observation that the corresponding linear slopes of benzoyl-substituted BAs remained unchanged when *para*-, *meta*-, *ortho*-, or *ortho,ortho*-methyls were introduced into the aniline moiety. It was therefore concluded that 1-AN enhanced the charge transfer in 1-NBAs and the proximity of its $^{1}L_a$ and $^{1}L_b$ states was suggested to be responsible. Results showed that the charge transfers in 1-NBAs and 2-NBAs were not the same and 1-AN and 2-AN as electron donors were different not only in electron donating ability but in shaping the charge transfer pathway as well.

Introduction

The photophysics of 1-aminonaphthalene (1-AN) derivatives has attracted much recent attention [1–7] since a notable radiationless internal conversion (IC) occurs with 1-dialkylaminonaphthalene,[2–6,8,9] which leads to increased quantum yield and prolonged lifetime with increasing solvent polarity. It was proposed that the IC occurred *via* vibronic coupling of the proximate $S_1(^1L_b)$ and $S_2(^1L_a)$ states (the proximity effect), in which S_1 is the emissive state involving intramolecular charge transfer (ICT).[2–6,8,9] Such a fast IC process was not observed for the corresponding 2-aminonaphthalene (2-AN) derivatives and was ascribed to the relatively large energy gap between $S_1(^1L_b)$ and $S_2(^1L_a)$, $\Delta E(S_1, S_2)$.[8,9] In these investigations the amino group in aminonaphthalenes was considered as the electron donor while the naphthyl moiety as the electron acceptor. It thus remains to be of interest to compare 1-AN and 2-AN as electron donors.

Charge transfer with benzanilide has been investigated since 1970's [10–20] by its dual fluorescence in non-polar solvent, in which aniline was defined as the electron donor and benzoyl as the electron acceptor. We recently showed that with benzoyl-substituted benzanilides (BAs, Scheme 1) the CT emission energies varied linearly with the Hammett constants of the substituents at the benzoyl moiety [eqn. (1)]:[20]

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

In eqn. (1) $E_{0,0}$ is the (0,0)-transition energy, δE_{rep} is the repulsion energy of the Franck-Condon ground state reached after
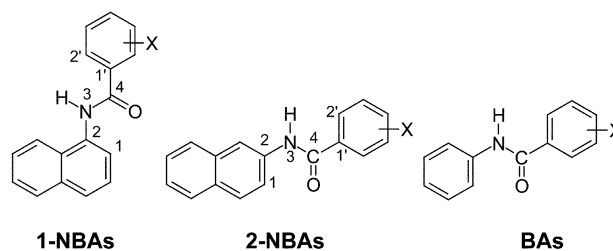
Scheme 1 Molecular structures of 1-NBAs, 2-NBAs and BAs. Substituents X's are (a) *p*–OC$_2$H$_5$, (b) *p*–CH$_3$, (c) H, (d) *p*–F, (e) *p*–Cl, (f) *p*–Br, (g) *m*–Cl, (h) *m*–NO$_2$, and (i) *p*–NO$_2$, respectively. The numbers shown in the structures were only used to define the dihedral angles.

CT emission, σ is the Hammett constant of the substituent, ρ is the reaction constant defined in the classic Hammett equation, and R and T are the gas constant and absolute temperature. The linear slope indicated the charge transfer extent in the CT state while the intercept indexed the electron donating ability of the un-substituted aniline moiety.[20] We therefore decided to employ the CT reaction in BAs to probe the difference of 1-AN and 2-AN as electron donors by preparing *N*-benzoylaminonaphthalene derivatives with substituent at the benzoyl moiety and examining the substituent effects on the charge transfer fluorescence.

In the present paper we report the synthesis and the fluorescence and absorption spectra in cyclohexane of *N*-(substituted-benzoyl)-1-aminonaphthalenes and 2-aminonaphthalenes

**Table 1** AM1 calculated ground-state structural parameters

	1-NBAs			2-NBAs		
	Dihedral angles/° [a]		Dipole moment/D	Dihedral angles/° [a]		Dipole moment/D
X	C1–C2–N3–C4	N3–C4–C1′–C2′		C1–C2–N3–C4	N3–C4–C1′–C2′	
p–OC$_2$H$_5$	25.8	40.9	3.43	9.8	41.5	3.53
p-CH$_3$	25.9	42.7	3.71	8.3	43.3	3.66
H	25.8	43.4	3.43	9.6	44.6	3.34
p–F	26.4	42.6	2.73	11.4	43.2	2.42
p–Cl	26.3	43.3	2.82	11.1	44.1	2.55
p–Br	26.4	43.8	2.79	11.2	44.6	2.49
m–Cl	26.2	43.5	2.53	10.1	43.0	2.41
m–NO$_2$	27.3	40.7	3.19	12.2	41.2	3.18
p–NO$_2$	27.4	45.4	4.61	12.0	45.5	4.22

[a] The atom numbers were assigned as shown in Scheme 1.

(1-NBAs, **1** and 2-NBAs, **2**, Scheme 1). We found all of the prepared amide derivatives, as benzanilides, emitted CT fluorescence in cyclohexane and the CT emission energy varied linearly with the Hammett substituent constant with the linear slope higher for 1-NBAs in which a full charge separation in the CT state was established. We showed that the charge transfer in 1-NBAs was more enhanced than in 2-NBAs and 1-AN and 2-AN were different not only in their electron donating abilities.

Experimental

N-(substituted-benzoyl)-1-aminonaphthalenes and 2-amino-naphthalenes (1-NBAs and 2-NBAs, Scheme 1) and the corresponding aniline derivatives (Scheme 2) were synthesized by the reaction in the presence of anhydrous Na$_2$CO$_3$ in diethyl ether of aminonaphthalenes or anilines with substituted benzoyl chlorides which were *in situ* prepared from corresponding benzoic acids and SOCl$_2$. All compounds were purified by repeated recrystallization from DMF/H$_2$O (10:1, v/v) for 1-NBAs or from acetone for 2-NBAs and aniline derivatives and were confirmed by IR (Nicolet Avatar FT-IR 360) and ^{1}H NMR (Varian Unity$^+$ 500MHz, DMSO-d$_6$, TMS) data. Solvents used for fluorescence and absorption spectra measurements were purified just before use and were checked to have no fluorescent impurity at the employed excitation wavelength.
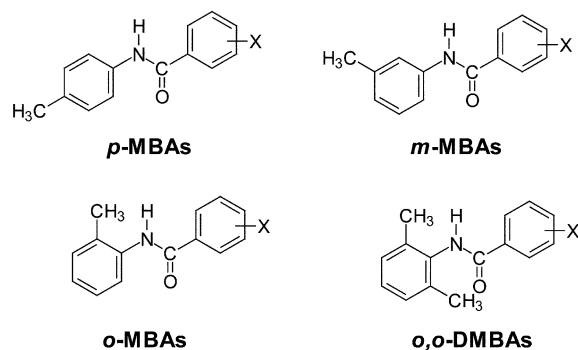
Scheme 2 Molecular structures of the methyl-substituted benzanilides

Corrected fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrometer with excitation wavelength of 310 nm for 1-NBAs, 300 nm for 2-NBAs and 280 nm for BAs derivatives by a xenon lamp of 150 W. The slits for both monochromators were 5 nm and a scan rate of 240 nm min^{-1} was chosen. Fluorescence quantum yields were measured using quinine sulfate as standard (0.546 in 0.5 M H$_2$SO$_4$, [ref. 21]). The absorption spectra were taken on Beckman DU-7400 or Varian Cary 300 UV-Vis spectrophoto-

meter using a 1-cm quartz cell. All spectra were measured at a sample concentration of *ca.* 10^{-5} M at room temperature (298 K).

The reduction potentials of 1-NBAs were measured by cyclic voltammetry on BAS-200 electrochemical analyzer (BAS, US) in a three-electrode configuration. The glass–carbon disc was employed as the working electrode, SCE as the reference electrode, and platinum wire as the counter electrode. The CV diagrams in ethanol–water (1:1, v/v) solutions were taken under N$_2$ by a scan rate of 0.1 V s^{-1} over the potential range of +1.0 V to −3.0 V. 0.25 M of (n-C$_4$H$_9$)$_4$NBr was used as the supporting electrolyte.

Ground-state geometrical structures were optimized by semi-empirical AM1 method using MOPAC (version 97.0) programs in Alchemy 2000 software package,[22] and the single-point calculations were performed by *ab initio* Hartree–Fock method using STO-3G basis sets in Gaussian 94 program,[23] denoted as HF/STO-3G//AM1.

Results and discussion

To avoid the steric effect introduced by the substituent, only *para*- and *meta*-substituted NBAs were synthesized. The single-point calculations indicated that *cis*-NBAs were *ca.* 3 kcal mol^{-1} higher in total energy than *trans*-NBAs, revealing that NBAs exist preferentially in *trans*-conformation, as BAs did.[17,20] The ground state structures of all *trans*-NBA derivatives were optimized with the AM1 method and the dihedral angles and the dipole moments were compiled in Table 1. It follows from Table 1 that the benzoyl substitution does not result in an obvious change in the ground-state structures within the same series, whereas the dihedral angle ∠C1–C2–N3–C4 of 1-NBAs is much higher than that in 2-NBAs, suggesting the steric effects of the substitution *ortho* to the amino group and/or of the *peri*-H at C-8 in 1-NBAs.

Fig. 1 shows the absorption spectra of 1-NBAs and 2-NBAs in cyclohexane. Obviously, the absorption spectra of 1-NBAs and 2-NBAs were much similar to those of 1-AN and 2-AN, and the main absorption bands could be ascribed to the ^{1}L$_a$ ← ^{1}A and ^{1}L$_b$ ← ^{1}A transitions, respectively.[8,9] The absorption of 1-NBAs peaked at 307 nm was found well mixed with that of the ^{1}L$_b$ ← ^{1}A transition that appeared as a shoulder at around 325 nm. With 2-NBAs, however, the broad absorption at *ca.* 298 nm originating from the ^{1}L$_b$ ← ^{1}A transition was obviously separated from the ^{1}L$_a$ ← ^{1}A absorption that lied at shorter wavelength (Fig. 1 and Table 2). It was noted that the position and shape of the absorption spectra within 1-NBAs and 2-NBAs series, respectively, were hardly affected when substituents were varied from electron-donating to electron-withdrawing groups at the *para*- or *meta*-positions of the benzoyl moiety (Fig. 1 and Table 2). The nitro-derivatives, as exceptions, had absorption tails extending to longer

Table 2 Spectroscopic data for 1-NBAs and 2-NBAs in cyclohexane

Comp.	λ_{abs}/nm	ε/M^{-1} cm^{-1}	λ_{flu}/nm	Fluorescence quantum yield
1a	307	16115	480	0.0029
1b	307	17127	502	0.0025
1c	307	21095	514	0.0019
1d	305	23523	508	0.0020
1e	307	17251	532	0.0016
1f	308	12798	536	0.0013
1g	308	11962	546	0.0010
1h	304	14876	—[a]	0.0003
1i	293/330	9966/6304	—[a]	<0.0001
2a	298	15621	476	0.0027
2b	298	11038	490	0.0044
2c	298	13071	500	0.0044
2d	297	8129	496	0.0053
2e	299	6616	514	0.0060
2f	303	8789	518	0.0044
2g	300	13315	530	0.0025
2h	308	8321	550	0.0012
2i	303	5372	555	0.0014

[a] Too weak to be estimated accurately.
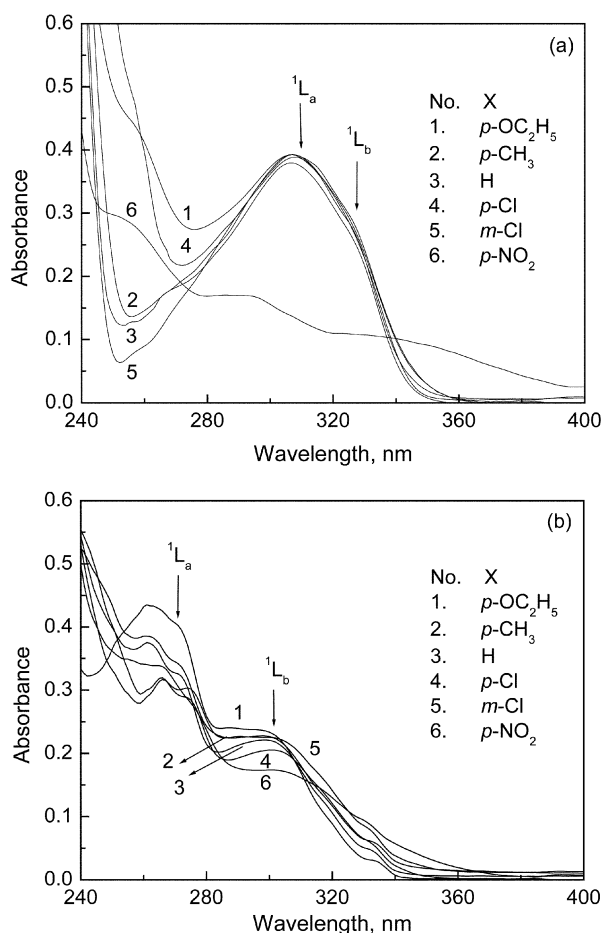
Fig. 1 Absorption spectra of (a) 1-NBAs and (b) 2-NBAs in cyclohexane

wavelength, probably indicating the occurrence of the ground state charge transfer, in particular with 1-NBAs (Fig. 1). The weak dependence of the absorption spectra on the substitution (Table 2) reflected the similarity of the locally excited (LE) state structure within the same series because of the similar ground-state structure suggested by the quantum mechanical calculations (Table 1). It is therefore not risky to assume that both $E_{0,0}$ and δE_{rep} remain constant within 1- and 2-NBA series, respectively, which means that eqn. (1) would hold for 1-NBAs and 2-NBAs for clarifying the charge transfer character as has been done with BAs.[20]

The fluorescence spectra of 1-NBAs and 2-NBAs in cyclohexane are shown in Fig. 2 in which it was seen that all of the NBA derivatives exhibited an abnormal long-wavelength fluorescence at around 500 nm and parts of them showed a very weak emission at about 370 nm. The short-wavelength band positions were noted to be close to those of 1-AN (373 nm) and 2-AN (372 nm) in n-hexane[24] and could result from the LE state or impurity that still remains to be elucidated, as also with benzanilide derivatives reported previously.[11-20] The long-wavelength fluorescence of 1-NBAs and 2-NBAs were found to shift to the red with increasing electron withdrawing ability of the substituent at the benzoyl moiety, and was therefore
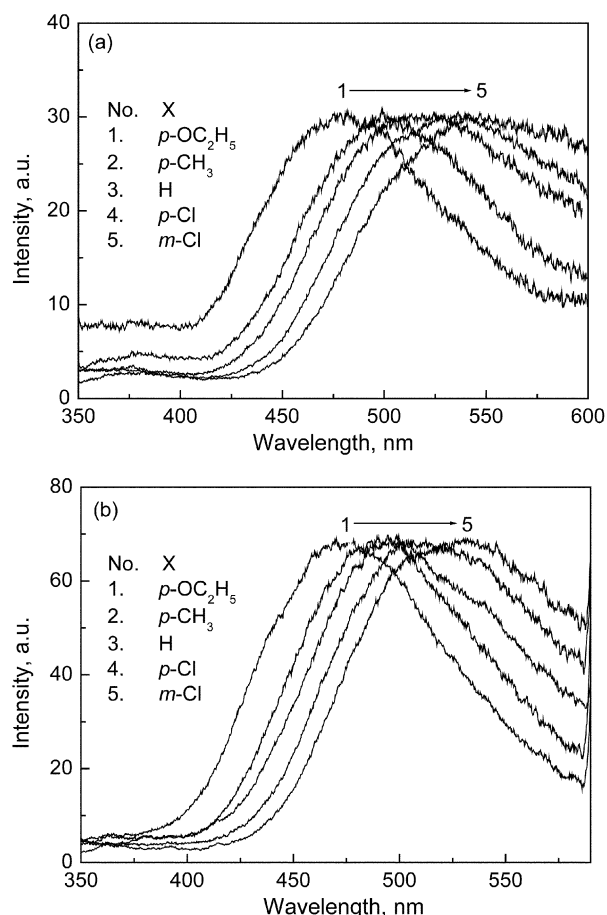
Fig. 2 Normalized fluorescence spectra of (a) 1-NBAs and (b) 2-NBAs in cyclohexane

assigned to the intramolecular charge transfer (ICT) state with aminonaphthalene and benzoyl moiety being electron donor and acceptor, respectively, as has been done similarly with BAs.[16–20] The CT nature was further supported by the observation of a substantial red shift of the long-wavelength emission with increasing solvent polarity, for example, the ICT emission of 1-NBA shifted from 514 nm in pure cyclohexane to 522, 546 and 558 nm, respectively, when 1, 5 and 20%(v/v) of diethylether was introduced into cyclohexane. Importantly, linear free energy correlations between the CT emission energies and the Hammett constants[25] of the substituents, as given in eqn. (1),[20] were indeed found with 1-NBAs and 2-NBAs series, respectively (Fig. 3). The value of the linear slope with 1-NBAs (-0.45 eV, $\gamma = -0.9583$, $n = 7$) was found to be higher than that with 2-NBAs (-0.35 eV, $\gamma = -0.9425$, $n = 7$), and the latter was close to that of the aniline derivatives (-0.345 eV).[20] This observation indicated that the charge transfer in 1-NBAs and 2-NBAs be different, with the latter being similar to that of BAs. The higher slope value suggested a higher charge separation extent in the CT state of 1-NBAs than in that of 2-NBAs.[20] This difference in the linear slopes for 1-NBAs and 2-NBAs could in principle result from the differences in the electron-donating abilities of 1-AN and 2-AN as electron donors and/or the steric effects in 1-NBAs due to the C-8 *peri*-H and the substitution *ortho* to amino group that are absent in 2-BNAs. The lower intercept in the linear correlation of 1-NBAs (Fig. 3) is actually indicative of the higher electron donating ability of 1-AN,[20] which is in agreement with the known data of lower oxidation potential of 1-AN than of 2-AN.[24]
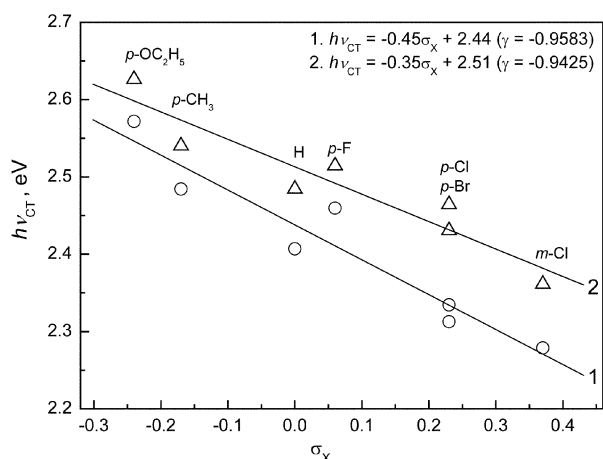

Fig. 3 The linear correlation between the CT emission energies in cyclohexane of (1) 1-NBAs and (2) 2-NBAs and the Hammett substituent constant

To clarify these factors, several series of benzanilide derivatives (Scheme 2) were prepared and the charge transfer reactions were similarly investigated. In those benzanilide derivatives methyl substituents were introduced into the aniline moiety for modifying the electron donating ability of the aniline donors (*para*- and *meta*-methyl, *p*-MBAs and *m*-MBAs, Scheme 2) and for introducing steric hindrance (*ortho*-methyls, *o*-MBAs and *o,o*-DMBAs, Scheme 2). The steric effect in the latter two series was shown by the dihedral angle $\angle$C1–C2–N3–C4, obtained from AM1 calculations, that increased from an average of 8.7 and 9.3° for *p*-MBAs and *m*-MBAs to 18.5° for *o*-MBAs and 62.5° for *o,o*-DMBAs.

It is significant to note that similar linear slopes (-0.35 eV) were found for the correlation between the CT emission energies and the Hammett constants for all of the four series of aniline derivatives (Fig. 4) and were also close to those of BAs (-0.345 eV)[20] and 2-NBAs (-0.35 eV, Fig. 3). This observation clearly suggested that both the differences in
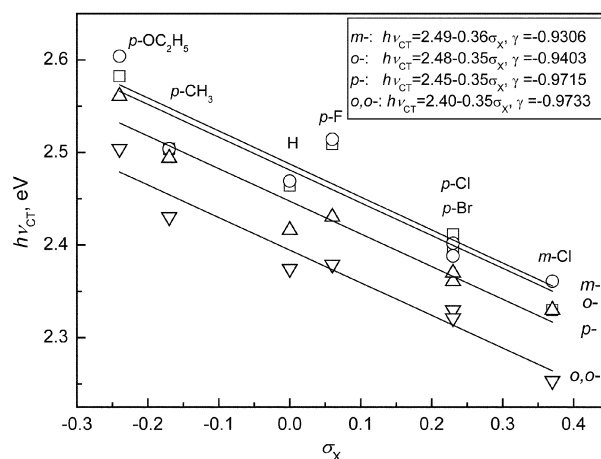

Fig. 4 The linear correlations of the CT emission energies of *p*-MBAs, *m*-MBAs, *o*-MBAs and *o,o*-DMBAs in cyclohexane against the Hammett substituent constant

the electron donating ability of the electron donor (aniline in BAs, *m*-methylaniline in *m*-MBAs and *p*-methylaniline in *p*-MBAs of enhancing electron donor, also suggested by decreasing intercept from 2.54,[20] 2.49 to 2.45 eV, Fig. 4) and in the steric effect (*p*-MBAs, *m*-MBAs, *o*-MBAs and *o,o*-DMBAs of increasing steric hindrance around the aniline amino group) did not result in obvious difference in the linear slope for the correlation between the CT emission energy and Hammett substituent constant. It was therefore made clear that the difference in the linear slopes for 1-NBAs and 2-NBAs was not due to the steric effect in 1-NBAs and the difference in electron donating ability of the donor. This means that 1-AN and 2-AN, as electron donors, differ not only in their electron donating abilities. The observation that the charge transfer in 2-NBAs was similar to that in BAs pointed to the similarity of 2-AN as electron donor to aniline. With 1-NBAs a higher extent of charge separation in the CT state was shown by a higher value of linear slope (-0.45 eV, Fig. 3), suggesting that 1-AN enhanced the charge transfer reaction in 1-NBAs. The charge separation extent in the CT state of 1-NBAs was further evaluated by correlating the CT emission energies with their reduction potentials. A linear dependence was found with a slope of -1.00 ($\gamma = -0.9229$, $n = 6$, Fig. 5), which indicated a full charge separation in the CT state of 1-NBAs, as assumed in exciplexes in nonpolar solvents by the Weller [eqn. (2)].[26]

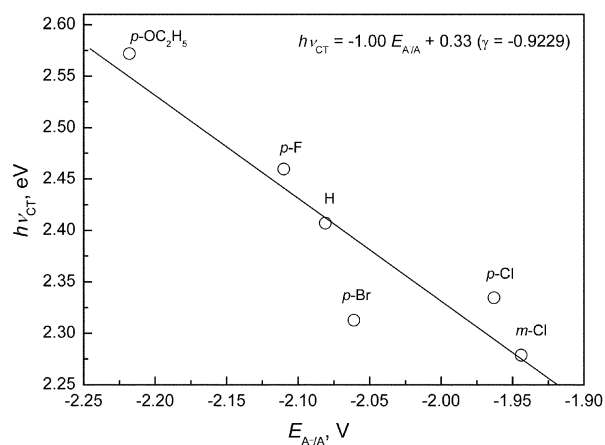$$h\nu_{CT} = E_D^{ox} - E_A^{red} - \delta E_{rep} + 0.15 \text{ eV} \qquad (2)$$

Fig. 5 Plots of the CT emission energies of 1-NBAs in cyclohexane against the reduction potentials of (**1a**) -2.218, (**1b**) not obtained, (**1c**) -2.081, (**1d**) -2.110, (**1e**) -1.963, (**1f**) -2.061 and (**1g**) -1.944 V.

In a discussion of the internal conversion in 1-AN and 2-AN derivatives the vibronic coupling of the $S_1(^1L_b)$ and $S_2(^1L_a)$ states has been invoked to be an important promoting factor.[2–6,8,9] This vibronic coupling has also been suggested as a reaction coordinate for the ICT in *p*-dimethylaminobenzonitrile (DMABN) and its derivatives.[27,28] We therefore tentatively assumed that the enhanced charge transfer observed for 1-NBAs than for 2-NBAs (Fig. 3) resulted from an enhanced vibronic coupling of the proximate $S_1(^1L_b)$ and $S_2(^1L_a)$ states in 1-AN than in 2-AN in which the two excited states are well separated[8,9] which was also indicated in the absorption spectra of 2-NBAs (Fig. 1b). This finding showed that 1-AN and 2-AN as electron donors were different in shaping the charge transfer pathway. It hence deserves to point out that the benzanilide-like CT reaction could indeed be employed to probe the difference between 1-AN and 2-AN as electron donors and might be extended to other aromatic amine donors.

Conclusions

A systematic study of *N*-(substituted-benzoyl)-1-amino-naphthalenes (1-NBAs) and *N*-(substituted-benzoyl)-2-amino-naphthalenes (2-NBAs) with substituents at the *para*- or *meta*-position of the benzoyl phenyl ring were carried out to identify the difference of 1-AN and 2-AN as electron donors using benzanilide-like charge transfer as a probe reaction. All of the derivatives were found to emit a Stokes-shifted charge transfer emission at around 500 nm in non-polar solvent cyclohexane. While the absorption showed very weak dependence on the substitution, the long-wavelength CT emission strongly shifted to the red with increasing electron-withdrawing ability of the substituent. The CT emission energies were found to correlate linearly with the Hammett substituent constants, and a higher slope was found for 1-NBAs (-0.45 eV) than for 2-NBAs (-0.35 eV) which was very close to that of the aniline derivatives, benzanilides(-0.345 eV),[20] which clearly pointed to a higher charge separation extent in the CT state of 1-NBAs in which a full charge separation was established by the linear dependence of the CT emission energy upon reduction potential that gave a slope of -1.00. A comparative investigation of the charge transfer in benzoyl-substituted BAs with methyl-substitution at the aniline moiety showed that the corresponding linear slope remained almost unchanged when *para*-, *meta*-, *ortho*-, or *ortho,ortho*-methyls were introduced into the aniline moiety (-0.35 eV). The possible contributions of the differences in the electron donating abilities of 1-AN and 2-AN and in the steric effect due to the C-8 *peri*-H and the *ortho*-substitution to the amino group in 1-NBAs were then ruled out. It was suggested that the enhanced charge transfer in 1-NBAs was due to the proximity of the ^1L_a and ^1L_b states in 1-AN that allows for a better vibronic coupling important for the charge transfer reaction. It was therefore shown that 1-AN and 2-AN as electron donors were different not only in electron donating ability but also in shaping the charge transfer coordinate.

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