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Intramolecular charge transfer with 4-(*N*-phenylamino)benzoic acid. The *N*-phenyl amino conjugation effect

Li-Hua Ma [a], Zhao-Bin Chen [b,*,1], Yun-Bao Jiang [a,*,2]

[a] *Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China*
[b] *Department of Chemistry, Shanxi University, Taiyuan 030006, China*

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Abstract

4-(*N*-phenylamino)benzoic acid (PhABA) was synthesized and its fluorescence spectra were recorded. In aprotic polar solvents, PhABA emitted strongly Stokes-shifted single-banded fluorescence with practically the same wavelength as that of 4-(*N*,*N*-diphenylamino)benzoic acid (DPhABA), indicative of the ICT character of the emissive state. 4-(*N*-isopropylamino)benzoic acid (iPrABA) showed single band emission however, sluggish response to the solvent polarity. In alkanols dual fluorescence of PhABA and DPhABA was observed but with different dependencies on alkanol structures. We concluded that ICT occurring with PhABA was due to the *N*-phenyl/amino conjugation effect. The work could be of help in understanding speciality of anilino moiety as electron donor compared to aliphatic amino group.

1. Introduction

Since the elucidation of dual fluorescence of 4-(dimethylamino)benzonitrile (DMABN) [1,2], the properties of this remarkable molecule and its dual fluorescent derivatives have fascinated chemists, and tremendous efforts [3–14] have been devoted to understanding their behavior during the process from the initially locally excited (LE) to the intramolecular charge transfer (ICT). The investigations of the influence of electron donor and/or acceptor on the CT process are then of great importance for the understanding of the CT photophysics.

4-(*N*,*N*-dialkylsubstituted)aminobenzoic acids (DAABA) emit dual fluorescence originated from LE and CT states in solvents more polar than alkanes, while the 4-(*N*-mono-*n*-alkyl) substituted derivatives such as methyl, ethyl, 1-butyl, 1-hexyl (AABA) show single emission from LE insensible to solvent polarity [15,16].

In comparison to many researches on the *N*-alkyl substituted aminobenzoic acid, the *N*-phenyl substituted counterparts are limited. Kakaš [17] and Greiner [18] pointed out that for triphenylamine and its derivatives, there is conjugation

* Corresponding authors.
E-mail addresses: zchen@sxu.edu.cn (Z.-B. Chen), ybjiang@xmu.edu.cn (Y.-B. Jiang).
[1] Fax: +86-351-7010688.
[2] Fax: +86-592-2185662.

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between the nitrogen lone pair electrons and the phenyl π-electrons. The whole molecule is a new chromophore with characteristic absorption and emission spectra. *N*-phenyl vs *N*-alkyl substitution of aromatic amines leads to superior performance in material chemistry (hyperpolarizability [19], hole transport [20,21], electroluminescence [21,22], etc.). 4-Aminodiphenylamine is a model of the polymer polyaniline [23] and research in [23] has been extended in another publication [24]. But few studies have been devoted to the effect of *N*-phenyl substitution on the excited-state behavior.

We then synthesized PhABA, DPhABA, iPr-ABA and ethyl 4-(*N*-phenylamino)benzoate (PhA-BEt) to provide new clues for the understanding of superiority of anilino moiety as an electron donor to an aliphatic amino group. A particular goal is to elucidate the nature of ICT enhanced by the *N*-phenyl amino conjugation effect.

2. Experimental

PhABA was synthesized by refluxing ethyl 4-(*N*-acetylamino)benzoate and iodobenzene. ^{1}H NMR (DMSO-d_6/TMS): δ(ppm) 6.94(m, 1H), 7.05(d, 2H), 7.18(d, 2H), 7.32(m, 2H), 7.78(d, 2H), 8.72(s, 1H), 12.26(s, 1H). DPhABA was achieved by oxidation of 4-(*N*,*N*-diphenylamino)benzaldehyde. ^{1}H NMR ($CDCl_3$/TMS): δ(ppm) 7.90 (d, 2H), 7.32(t, 4H), 7.15(m, 6H), 6.99(d, 2H). iPr-ABA was obtained by the reaction of 4-aminobenzoic acid with 2-bromopropane. ^{1}H NMR (DMSO-d_6/TMS): δ(ppm) 1.14(d, 6H), 3.60(m, 1H), 6.26(d, 1H), 6.54(d, 2H), 7.65(d, 2H), 11.90(s, 1H). Organic solvents for spectral investigations were purified before use.

Absorption and corrected fluorescence spectra were recorded on Beckman DU-7400 absorption spectrophotometer and Hitachi F-4500 fluorescence spectrometer, respectively. The fluorescence quantum yields of the aerated sample solutions were measured by comparison with a quinine sulfate solution (0.546 in 0.5 mol l^{-1} H_2SO_4 [25]) of equal optical density at the excitation wavelength. NMR data were taken on Varian Unity$^+$ 500 MHz spectrometer. Ground-state structures of the investigated molecules were optimized by AM1 calculations [26].

3. Results and discussion

3.1. Spectral behavior of PhABA and DPhABA in aprotic solvents

3.1.1. Absorption spectra

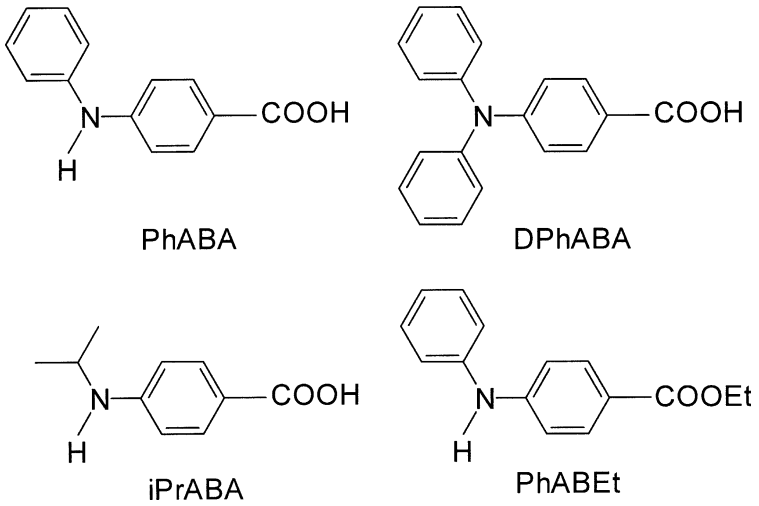
The absorption spectra of PhABA displayed a single broad band with a maximum of ca. 319 nm in different solvents, whereas DPhABA had two bands, one broad band at 335 nm and the other slightly narrower band at 300 nm with vibration structure (Table 1). This difference in the absorption spectra may be attributed to a larger separation between the two lowest absorption bands (L_a and L_b) [27]. The second band of DPhABA around 300 nm is the consequence of an electronic transition mainly localized in the triphenylamine moiety [28,29].

3.1.2. Fluorescence spectra

Compared to the diverse in ground-state, the fluorescence spectra of DPhABA and PhABA differed much in the same aprotic solvent. The fluorescence spectra of PhABA (Scheme 1) in aprotic solvents of varying polarity are depicted in Fig. 1a. PhABA, though among the *N*-monosubstituted derivatives of *p*-aminobenzoic acid (ABA), showed also the single emission band, however, red-shifted greatly with increasing the solvent polarity, together with gradually widening of the half-peak width (Table 1), in contrast to a polarity insensitive nature of the UV–Vis absorption and fluorescence excitation spectra (the figures were abbreviated). For example, the emission wavelength was red-shifted for 115 nm from 371 nm in cyclohexane (CHX) to 486 nm in acetonitrile (ACN) (Table 1). This is ascribed to the ICT nature of the emissive state. It should be pointed out that the maximal emission wavelength and the shape were independent of concentration and excitation wavelength from 280 to 340 nm. The solvent effect of PhABA differs much from that of AABA, which emits the short wavelength fluorescence solely from LE state hardly dependent on solvent polarity [15].

Table 1
The maximal absorption wavelength λ_{max}^{abs}, emission wavelength λ_{max}^{flu}, fluorescence quantum yield Φ, and full-width at half maximum (FWHM) of PhABA and DPhABA in aprotic solvents

Molecule	Solvent	E_T [30] (kcal mol^{-1})	λ_{max}^{abs} (nm)	λ_{max}^{flu} (nm)	Φ	FWHM (cm^{-1})
PhABA	CHX	30.9	316	371	0.365	4577
	DEE	34.5	320	413	0.308	5014
	DOX	36.0	321	425	0.316	5023
	THF	37.4	319	431	0.195	5032
	EtAc	38.1	320	438	0.166	5070
	$CHCl_3$	39.1	320	466	0.105	5102
	CH_2C1_2	40.7	316	473	0.125	5118
	ACN	45.6	316	486	0.033	5410
DPhABA	CHX	30.9	342, 299	401	0.228	3588
	DEE	34.5	321, 302	412	0.284	3909
	DOX	36.0	334, 303	423	0.317	4029
	THF	37.4	332, 303	428	0.341	4100
	EtAc	38.1	331, 302	434	0.354	4131
	$CHCl_3$	39.1	340, 305	465	0.509	4217
	CH_2Cl_2	40.7	339, 304	472	0.468	4248
	ACN	45.6	330, 302	481	0.215	4664
iPrABA	CHX	30.9		324		3588
	DEE	34.5		331		3909
	DOX	36.0		332		4029
	THF	37.4		334		4100
	EtAc	38.1		334		4131
	$CHCl_3$	39.1		335		4217
	CH_2Cl_2	40.7		343		4248
	ACN	45.6		352		4664



Scheme 1. Chemical structures of interested ABA derivatives.

To understand further the luminescence behavior of PhABA, DPhABA (Scheme 1) as one of the 4-(*N*,*N*-disubstituted)aminobenzoic acid derivatives which should possess ICT characteristics was synthesized. Fig. 1b shows the fluorescence spectra of DPhABA in the same series of aprotic

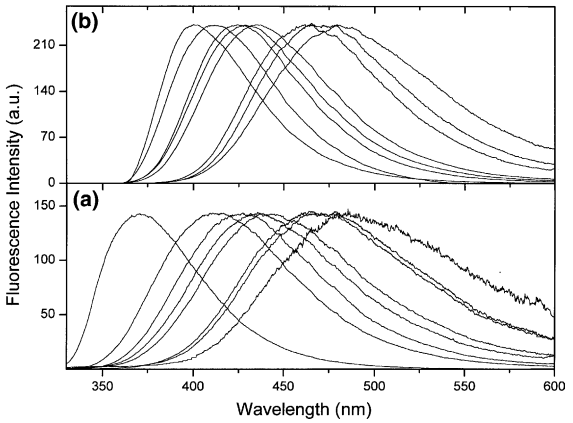


Fig. 1. The fluorescence spectra of (a) PhABA and (b) DPhABA in organic solvents. From left to right the solvents are cyclohexane (CHX), diethyl ether (DEE), dioxane (DOX), tetrahydrofuran (THF), ethyl acetate (EtAc), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and acetonitrile (ACN), respectively.

solvents. DPhABA exhibits sole emission band, which is red-shifted with increasing solvent polarity (Fig. 1b, Table 1). It is significant that the maximal emission wavelengths (λ_{max}^{flu}) of DPhABA and PhABA are almost the same in each polar solvent such as diethyl ether (DEE), tetrahydrofuran (THF), dioxane (DOX), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and ACN. The only difference occurs in nonpolar solvent CHX in which the λ_{max}^{flu} of PhABA (371 nm) is obviously shorter than that of DPhABA (401 nm). In addition, the half-peak width of PhABA in each solvent is ca. 1000 cm^{-1} broader than that of DPhABA (Table 1). The introduction of another phenyl in DPhABA made the amine less distorted, which resulted in the red-shift of absorption and fluorescence in CHX (Table 1) and the narrower band of the emissive fluorescence [28]. The fluorescence quantum yields of PhABA are increasingly lower with increasing solvent polarity (0.365 in CHX compared to 0.033 in ACN), whilst solvent polarity has far less effect on the quantum yields of DPhABA (0.228 in CHX and 0.215 in ACN). Despite the differences, the similarity of the emission wavelength of PhABA and DPhABA in aprotic polar solvents supported the ICT nature of PhABA emissive state.

Two assumptions are proposed for the ICT emission of PhABA. One is the twisting of *N*-phenylamino with respect to the benzoic acid moiety which resulted from steric hindrance according to TICT model, just as in the case of the ICT model compound 3,5-dimethyl-4-(*N*,*N*-dimethylamino)benzonitrile (MMD) (Scheme 2) [2,3], the other is the *N*-phenyl amino conjugated effect [28].

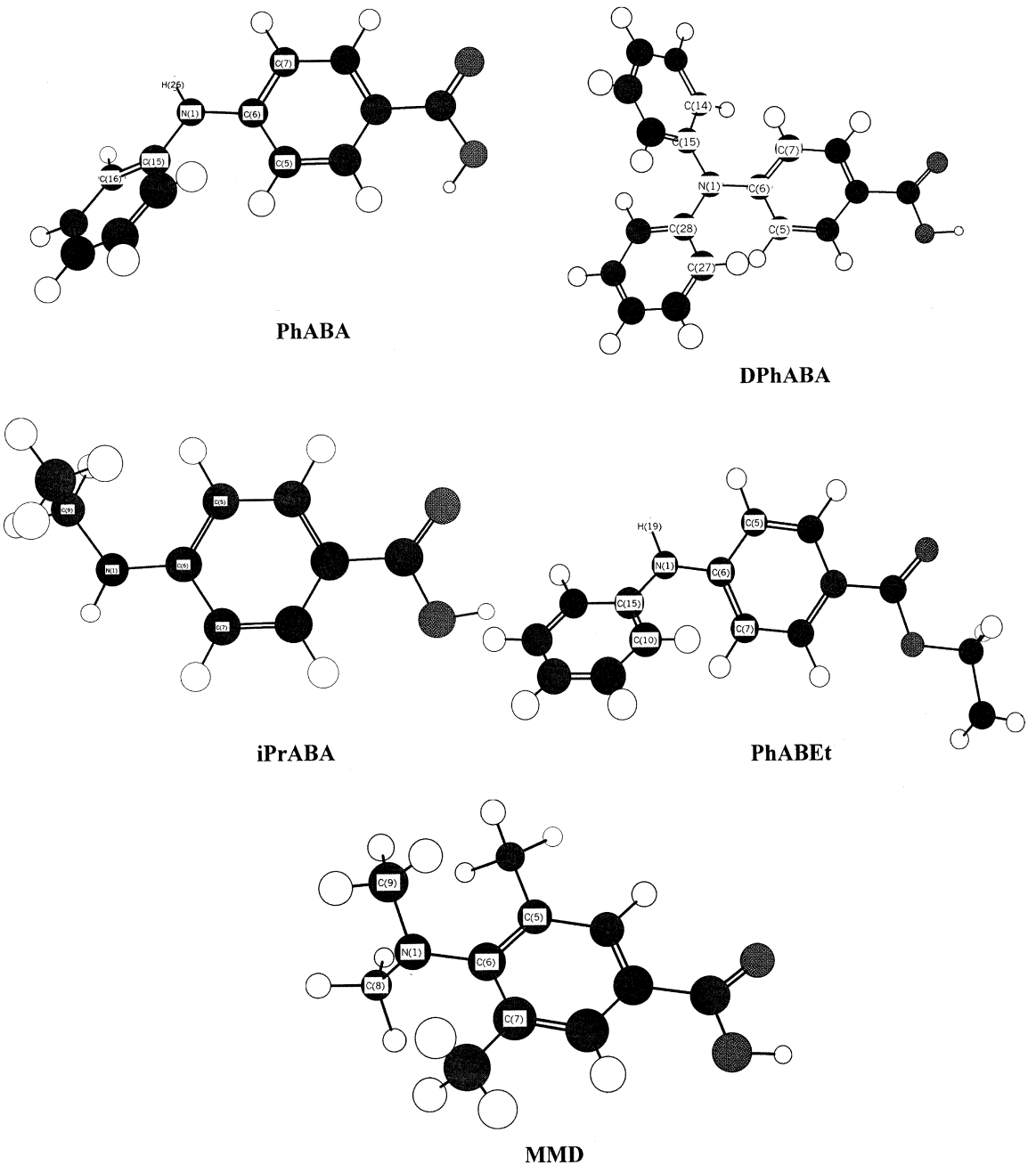
3.2. Molecular structures of PhABA and DPhABA

The ground-state structures of PhABA and DPhABA were optimized using AM1 calculation. The optimized structures are shown in Scheme 2 and the structural parameters are reported in Table 2. For PhABA, the dihedral angle of C15–N1–C6–C7 equals 1.4°, whereas C16–C15–N1–C6 of 53.3° is found. For DPhABA, the dihedral angle of C15–N1–C6–C7 is 26.8°, of C28–N1–C6–C7 is 27.2°, of C27–C28–N1–C6 is 40.5° and of C14–C15–N1–C6 is 38.9°. The twist of the amino group leads to a small lengthening of the *N*-phenyl bond by the theory calculation. The N1–C6 bond lengths are 1.394 and 1.404 Å for PhABA and DPhABA, respectively. As compared with ICT model compound MMD (Scheme 2) which shows only CT band owing to the great steric effect by methyls, the corresponding dihedral angles of C8–N1–C6–C7 and C9–N1–C6–C7 are 51.5° and 87.3°, respectively, with 1.430 Å bond length of N1–C6. Though the AM1 method is rough, the results of computation show at least that the steric hindrance effects of PhABA and DPhABA are different, both lower than that of MMD. The steric hindrance effect, therefore, is not the key accounting for the ICT emission behavior of PhABA in polar solvents.

3.3. Counter evidences of N-phenyl amino conjugation

3.3.1. The emission characters of iPrABA

We postulated that the role of *N*-phenyl amino conjugation could be proved or disproved conclusively by studying the fluorescence spectra of iPrABA (Scheme 1) (Fig. 2). iPrABA was selected because its steric structure around amino group



Scheme 2. AM1 optimized ground-state structures of related compounds.

was expected to be similar to that of PhABA, whereas its lone pair electrons at the amino nitrogen was far less delocalized when compared to that of PhABA. The amino conjugation would be disrupted and hence the role of *N*-phenyl amino conjugation in ICT process would be proved to some extent if no CT of iPrABA was discerned. Fig. 2 and Table 1 showed that the λ_{max}^{flu} of iPrABA

Table 2
AM1 calculated dihedral angle at the amino conjunction moiety, bond length, ground-state dipole moment μ_g, the measured CT state dipole moment μ_e^{CT} and Onsager radius R

Molecule	Dihedral angle[a] (°)		Bond length (Å)			μ_g (D)	μ_e^{CT} (D)[b]	R[c] (Å)
PhABA	C16–C15–N1–C6	C15–N1–C6–C7	N1–C6	N1–C15	N1–H26	3.73	17.4	4.26
	53.3	1.4	1.394	1.410	0.998			
DPhABA	C28–N1–C6–C7	C15–N1–C6–C5	N1–C6	N1–C15	N1–C28	3.49	18.4	4.54
	27.2	26.8						
	C27–C28–N1–C6	C14–C15–N1–C6	1.404	1.417	1.417			
	40.5	38.9						
PhABEt	C10–C15–N1–C6	C15–N1–C6–C7	N1–C6	N1–C15	N1–H19	3.09	17.7	4.36
	53.6	1.6	1.396	1.408	0.995			
iPrABA	C9–N1–C6–C7		N1–C6	N1–C9	N1–H	4.36	9.6[d]	4.09
	21.5		1.392	1.450	0.998			
MMD	C9–N1–C6–C7	C8–N1–C6–C7	N1–C6	N1–C9	N1–C8			
	87.3	51.5	1.430	1.441	1.441			

[a] The atom numbers are indicated in Scheme 2.
[b] Measured from solvatochromic data, see details in the text.
[c] Calculated at HF/STO-3G level.
[d] The dipole moment of LE state.

was blue-shifted compared to that of PhABA (Fig. 1a) and red-shifted slightly with increasing solvent polarity, from 324 nm in CHX to 343 nm in ACN (Table 1). The solvent effect findings of iPrABA and PhABA differ much, which could be seen more clearly by the plots of the emission energies $h\nu^{max}$ against polarity scale $f - f'$ (Fig. 3). The red-shift with increasing solvent polarity experienced by the emission band of iPrABA is approximately of the same magnitude as that found for the LE band of 4-(*N*-methylamino)benzenitrile (MABN) and DMABN [16]. The solvent polarity dependence of the emission bands of PhABA and DPhABA is just like that of the CT band of DMABN, clearly demonstrating the dramatic difference between the emission characters of PhABA and iPrABA. The CT state dipole moments were estimated from the solvatochromic

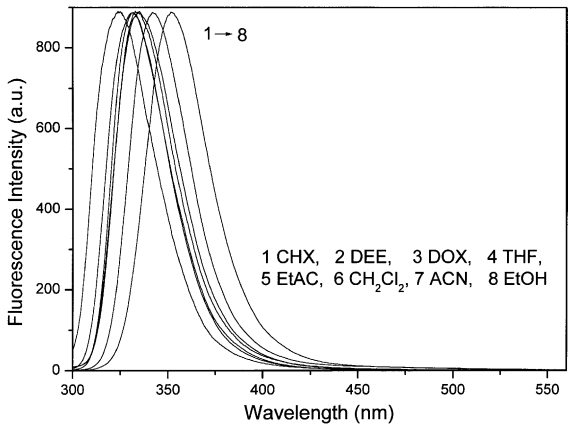


Fig. 2. The fluorescence spectra of iPrABA in solvents of different polarity.

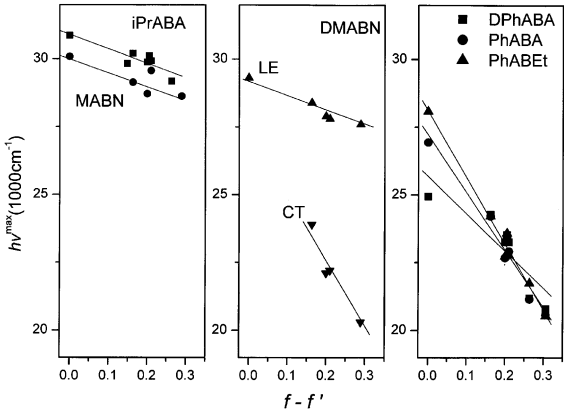


Fig. 3. Solvatochromic plots of the energies $h\nu^{max}$ of the LE fluorescence of MABN, iPrABA, DMABN and also of the ICT emission of DMABN, DPhABA, PhABA and PhABEt. $f - f'$ is solvent polarity parameter. The data in chloroform were not included in the linear fitting.

data following a reported method [16] by plotting the CT emission energies against those of DMABN in corresponding solvents. The ground and CT state dipole moments of DMABN, 6.6 and 17 D, respectively, were taken [23]. The radiuses of PhABA, DPhABA and iPrABA were calculated at HF/STO-3G level to be 4.26, 4.54 and 4.09 Å (Table 2), respectively. The excited-state dipole moments of PhABA, DPhABA and iPrABA are 17.4, 18.4 and 9.6, respectively. However, it should be noted that the oxidation potential of aniline (1 V) is lower than that of *N*-alkylamine (1.4 V) favoring thermodynamically the intramolecular electron transfer in PhABA. We therefore provided another forceful counter evidence to illuminate the *N*-phenyl amino conjugation, the fluorescence spectra of PhABA and DPhABA in protic solvents.

3.3.2. Fluorescence spectra of PhABA and DPhABA in protic alkanols

We assumed that if the excited-state delocalized electron shared by conjugated system of nitrogen and phenyl moiety that means a tremendously larger CT character for the *N*-phenyl derivatives in the lowest excited-state was right, changing solvent from aprotic to protic such as methanol (MeOH), the hydrogen bond between nitrogen of PhABA or DPhABA and hydroxyl of MeOH would decrease conjugation effect between nitrogen and *N*-phenyl. Fluorescence of PhABA and DPhABA from LE might emerge.

The fluorescence spectra of PhABA (a) and DPhABA (b) in alkanol solvents were recorded (Fig. 4) and the spectral data were in Table 3. The emission band was found greatly blue-shifted. As for PhABA in MeOH ($f - f'$ is 0.309), only an

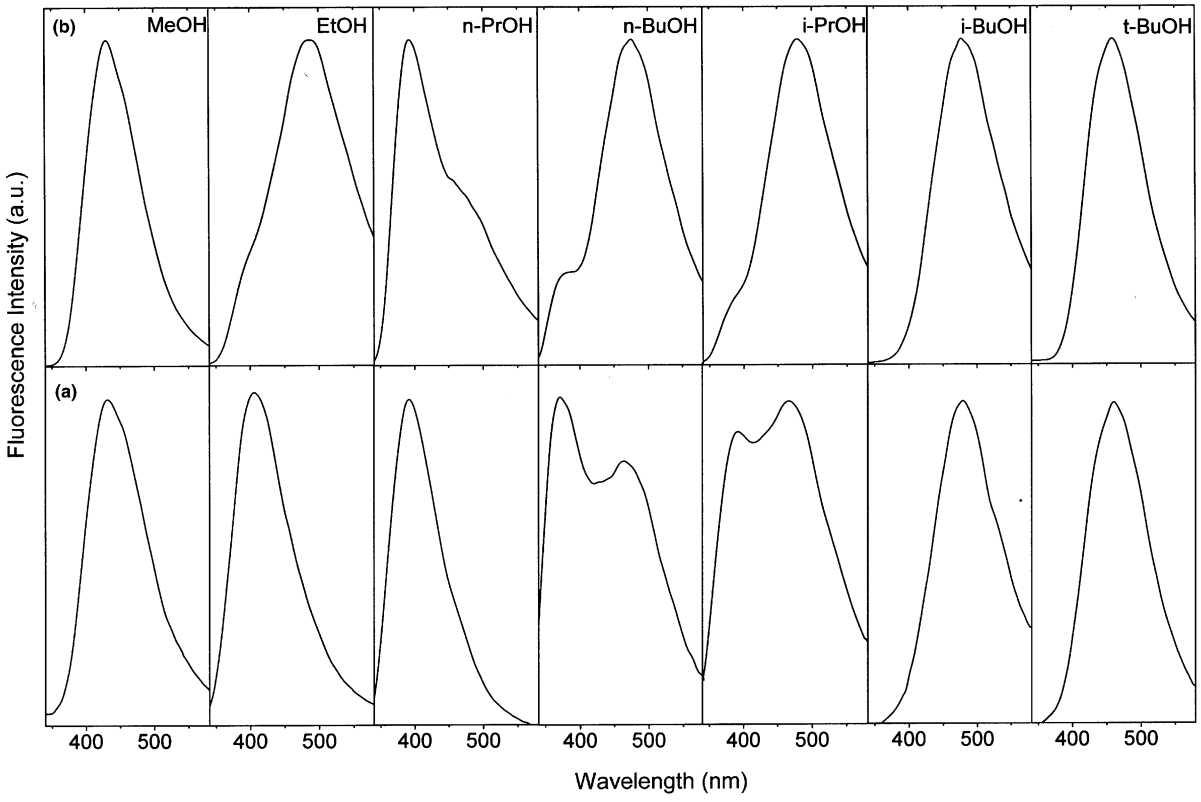


Fig. 4. The fluorescence spectra of (a) PhABA and (b) DPhABA in alkanols. From left to right the solvents are methanol (MeOH), ethanol (EtOH), normal propanol (n-PrOH), normal butanol (n-BuOH), iso-propanol (i-PrOH), iso-butanol (i-BuOH), and tert-butanol (*t*-BuOH), respectively.

emission band located at ca. 430 nm was observed, compared with 486 nm in ACN ($f - f'$ is 0.305). The result is in agreement with the fact that MeOH is the easiest alkanol to form hydrogen bond with nitrogen [30]. Changing the solvent from MeOH to ethanol (EtOH), normal propanol (n-PrOH), normal butanol (n-BuOH), iso-propanol (i-PrOH), iso-butanol (i-BuOH) and tert-butanol (*t*-BuOH), with decreased ability to form hydrogen bond, would decrease the ability of alkanol hydroxyl to affect *N*-phenyl amino conjugation, thus relatively enhancement of ICT emission component would be observed. It was found in Fig. 4a that the ICT emission of PhABA did not emerge in solvents of MeOH, EtOH and n-PrOH until the solvent was n-BuOH. The intensity ratio of long wavelength to short wavelength bands was increasingly larger when the solvent became more difficult to form hydrogen bond owing to the steric hindrance. For example, in *t*-BuOH that was the most difficult to form hydrogen bond owing to large steric effect introduced by methyls, the emission consisted mainly of ICT state. The similar results were obtained with DPhABA. Dual fluorescence of DPhABA was observed in EtOH, the position of the short wavelength band was just about the same with DPhABA in CHX, while the long wavelength band was the ICT emission (Fig. 4b). Also, the intensity ratio of long wavelength to short wavelength bands was increasingly larger (Table 3) when the solvent became more difficult to form hydrogen bond.

Just as in aprotic solvents, the half-peak width of PhABA was larger than that of DPhABA. The fluorescence maximum wavelengths of PhABA and DPhABA in different alkanol solvents were almost the same except in EtOH and n-PrOH. It is easily interpreted that DPhABA, possessing two phenyl substituents at the amino group, is more difficult to form hydrogen bond with alkanols than PhABA. The hydrogen bond effect for DPhABA is hence not so great as that for PhABA.

Yoon and Kim et al. [31,32] have reported the hydrogen-bonding effect on the twisted intramolecular electron transfer (TICT). In [32], the effect of hydrogen bonding between hydroxyl group of SiO_2 colloid (polarity of its surface is similar to that of EtOH) and *p*-*N*,*N*-dimethylaminobenzoic acid (DMABA) on the latter's TICT was investigated in detail. The SiO_2-concentration dependent intensity ratio of the TICT to the LE emission clearly showed that an enhancement of the TICT emission occurred upon addition of up to 0.3 μM of SiO_2 colloid whereas a reduction in that ratio took place in the presence of excess amount of SiO_2 colloid. The authors [32] considered that the

Table 3
The emission wavelength λ, CT to LE intensity ratio, I_{CT}/I_{LE}, the total quantum yield $\Phi_{f,total}$ the absorption wavelength λ_{max}^{abs} of PhABA and DPhABA in alkanols

Molecule	Solvent	E_T [30] (kcal mol^{-1})	$f - f'$	λ_{CT} (nm)	λ_{LE} (nm)	I_{CT}/I_{LE}	$\Phi_{f,total}$	λ_{max}^{abs} (nm)
PhABA	MeOH	55.4	0.309	–	432	–	0.028	315
	EtOH	51.9	0.289	–	406	–	0.036	324
	n-PrOH	50.7	0.274	–	391	–	0.031	321
	n-BuOH	50.2	0.264	477	391	1.0	0.030	320
	i-PrOH	48.6	0.276	471	371	0.8	0.052	324
	i-BuOH	47.2	0.266	479	–	7.9	0.057	324
	t-BuOH	43.3	0.251	460	–	16	0.074	324
DPhABA	MeOH	55.4	0.309	–	430	–	0.033	308
	EtOH	51.9	0.289	487	396	0.8	0.064	331, 300
	n-PrOH	50.7	0.274	479	396	0.5	0.073	332, 300
	n-BuOH	50.2	0.264	478	380	4.2	0.116	332, 300
	i-PrOH	48.6	0.276	476	380	5.9	0.227	333, 300
	i-BuOH	47.2	0.266	479	–	45	0.320	334, 300
	t-BuOH	43.3	0.251	456	–	152	0.601	335, 300

main reason for the emission enhancement and reduction was the different hydrogen-bonding sites. When SiO_2 concentration was low, hydrogen bonding was suggested to occur between the carboxylic group of DMABA and SiO_2 colloid. At higher SiO_2-colloid concentration, the hydrogen bonding was between the amino nitrogen of DMABA and the colloid. The latter is consistent with our conclusion that the hydrogen bonding is between the amino nitrogen of PhABA or DPhABA and the hydroxyl group of alkanol because the molar concentration of hydroxyl group is obviously high when alcohol is chosen as the solvent. In order to know clearly whether the hydrogen-bonding effect on *N*-phenyl (PhABA, DPhABA) and *N*-alkyl (DMABA) was the same or not, we investigated the effect of minute amount of EtOH in aprotic nonpolar solvents with these compounds. Fig. 5 shows the maximal emission wavelength (PhABA for example) as a function of EtOH volume fraction in DEE. It was observed that the maximal emission wavelength of PhABA, an *N*-phenyl substituted ABA, in DEE shifted to the red when a small amount of EtOH was introduced and remained constant over a medium EtOH concentration range that was followed by a substantial blue-shift at much higher EtOH concentration. In addition, the maximal emission wavelength of PhABA in absolute EtOH is 396 nm (Fig. 4). It should be noted that the hydrogen bond introduced by SiO_2 colloid affected only the intensity ratio of the dual fluorescence of DMABA while the emission wavelengths of both the LE and CT bands remained almost constant [32]. That means in the case of DMABA, no large blue or red-shift of the emission bands is observed upon hydrogen-bonding. The results lead to the conclusion that the hydrogen-bonding effect on the emission of DMABA, an *N*-alkyl substituted ABA, is different from that of PhABA, an *N*-phenyl substituted ABA. This, on the other side, supports our conclusion that it is the amino nitrogen of PhABA or DPhABA and the hydroxyl group of the alcohol solvent that form hydrogen bonds which hinder the *N*-phenyl/amino conjugation and hence lead to abnormally large blue-shift in the CT emission in alcohol solvents compared to that in aprotic solvent of similar polarity.

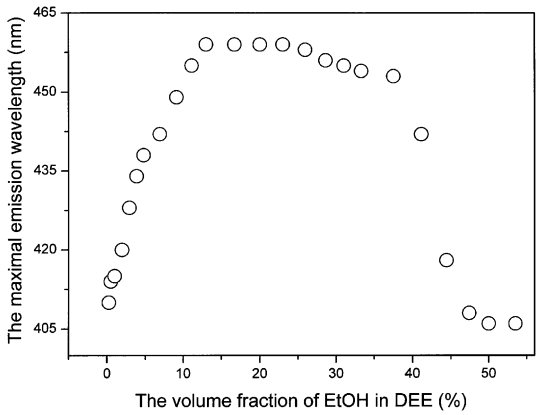


Fig. 5. The maximal emission wavelength of PhABA in DEE as a function of EtOH volume fraction.

PhABEt (Scheme 1) was synthesized in order to highlight further the hydrogen bond would be between nitrogen of DPhABA or PhABA and hydroxyl of alkanol. Similar phenomena were observed with PhABEt (Scheme 2) that had dipole moments of 17.7 (Table 2). For PhABEt, the emission wavelengths in different aprotic solvents were just as those for PhABA and DPhABA except 356 nm in CHX, clearly seen in Fig. 3.

4. Conclusions

The singlet emission band of PhABA in polar aprotic solvents is found to be typical of ICT character, which is quite different from the *N*-alkyl derivative. Introduction of another *N*-phenyl to PhABA, leading to is DPhABA, has little effect on the maximal emission wavelength and shape in polar aprotic solvents whilst much difference occurs in absorption spectra. We concluded that the delocalization of lone pair electrons of nitrogen conjugated to π electron of phenyl group might be the direct reason for the anomalous emission behavior of PhABA. Two approaches were used to disrupt the conjugation. The first approach involved the synthesis of a new model compound, in which *N*-phenyl of PhABA was placed by *N*-isopropyl. It is appealing that the emission behavior of iPrABA differs much to that of PhABA. In the second one, alkanols were introduced as the protic

solvent hydroxyl of which would form hydrogen bond with nitrogen of *N*-phenyl derivatives. Dual fluorescence was observed for both PhABA and DPhABA but with different dependencies on alkanol steric structures. The described experiments were designed counter evidently to ascertain that ICT could be enhanced by *N*-phenyl amino conjugation, which was supplement to the active researches on *N*-phenyl effect [28,33,34] and offered a new hint for constructing CT-based fluorescent chemosensors.

Acknowledgements

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