Substituent Effect on the Dual Fluorescence of Benzanilides and *N*-Methylbenzanilides in Cyclohexane. Direct Evidence for Intramolecular Charge Transfer

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Received: October 16, 2001; In Final Form: March 19, 2002

A series of benzoyl para- and meta-substituted benzanilides (BAs) and *N*-methylbenzanilides (MBAs) were synthesized and their absorption and fluorescence spectra in nonpolar solvent cyclohexane were investigated. Quantum mechanical calculations indicated that the ground state BAs existed preferentially in the trans configuration, whereas MBAs existed in the cis configuration, and benzoyl substitution hardly changed the ground-state structure in the same series. It was observed that all of the synthesized compounds displayed dual fluorescence in cyclohexane, i.e., a normal emission at ca. 330 nm and an abnormal long-wavelength fluorescence at around 500 nm. Although the normal emission of both BAs and MBAs did not show obvious variation, the long-wavelength emission shifted strongly to the red with increasing electron-withdrawing ability of the substituent at the benzoyl moiety. The emission energies of the long-wavelength fluorescence of BAs and MBAs in cyclohexane were found to vary linearly with the Hammett substituent coefficient σ with almost the same slopes of −0.34 eV for both lines. In diethyl ether, similar linear correlation was also found for BAs with a slope of −0.36 eV that is close to that in cyclohexane. It was concluded that the long-wavelength emission of both BAs and MBAs in cyclohexane originated from a single intramolecular charge transfer state of similar configuration for both BAs and MBAs and of high extent of charge separation. The latter was supported by a linear slope of −0.67 for the correlation of long-wavelength emission energies of BAs against their reduction potentials. It was suggested that the reaction constant ρ might reflect the extent of charge separation of the CT reaction and the ρ value for a full charge separation was calculated to be −8.5 and +8.5 for a substituent at the electron donor and acceptor moiety, respectively.

1. Introduction

The abnormal emission behavior of benzanilide (BA) in an EPA glass at 77 K was first reported by O'Conell et al.[1] in the early 1970s but did not received much attention until 1987 when Kasha and co-workers[2,3] reported their observation of the dual fluorescence of BA at room temperature in nonpolar fluid methylcyclohexane (MCH). The weaker and short wavelength emission was attributed to the locally excited (LE) state, whereas the stronger and abnormally long wavelength emission with a large Stokes shift was assigned to the photoinduced proton transfer (PT) state formed from the tautomerization within hydrogen-bonded dimer.[2] This PT model was immediately revised[3a] in a subsequently report of the observation of similar Stokes shifted long-wavelength fluorescence from *N*-methylbenzanilide (MBA) in which the PT channel was blocked. The long-wavelength emission of MBA was then suggested to originate from the intramolecular charge transfer (CT) state, whereas that of BA was ascribed to the overlapped emission from a PT state and a CT state.[3a] This assignment has been supported by Heldt et al.[4] and Lucht et al.,[5] but with modified source for the PT state of BA. The new version assumed that the PT state was formed from the intermolecular hydrogen-bonded aggregates formed from the hydrophilic *trans*-BA in a hydrophobic environment such as in hexane.[5] Azumaya et al.[6] and Lewis et al.,[7] on the other hand, concluded that the long-wavelength emission from both BA and MBA originated from a twisted intramolecular charge transfer (TICT) state with twisting occurring at the amide C−N bond between the anilino moiety (the electron donor) and the benzoyl moiety (the acceptor). It is obvious that discrepancy exists on the assignment of the Stokes-shifted long-wavelength emission of BA.

The original proposal of the CT origin of the long-wavelength emission with BA and MBA[3a] was based mainly on an analogy to the assignment made with the well-known dual fluorescent *p*-dimethylaminobenzonitrile (DMABN)[8] and was supported by a moderate solvatochromic shift observed with the MBA long-wavelength emission. It should be pointed out, however, that care needs to be taken in using this solvatochromic method that has been routinely employed for identifying the ICT character of the emissive state, because with MBA and BA the number of the solvents that can be used was very limited. For BA and MBA only solvents within the solvent polarity range of hexane to tetrahydrofuran (THF) could be used, in more polar solvent the long-wavelength emission was completely quenched.[2,3] Meanwhile, the photoinstability of BA and MBA[9] made it difficult to abstract credible messages from the time-resolved fluorescence investigations.[3d,6] It thus seems necessary to find

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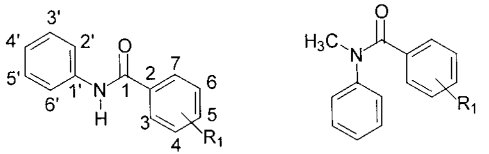
10.1021/jp013836c CCC: $22.00

SCHEME 1: Structures of the Benzoyl-Substituted Benzanilides (BAs, 1a−9a) and *N*-Methylbenzanilides (MBAs, 1b−9b)



R_1 =		
p-OC_2H_5	**1a**	**1b**
p-CH_3	**2a**	**2b**
H	**3a**	**3b**
p-F	**4a**	**4b**
p-Cl	**5a**	**5b**
p-Br	**6a**	**6b**
m-Cl	**7a**	**7b**
m-NO_2	**8a**	**8b**
p-NO_2	**9a**	**9b**

alternative methodologies to bring about new and direct evidences for understanding the origin of the long-wavelength emission observed with BA and MBA.

We attempted such an alternative method by systematic variations of the redox properties of the electron donor/acceptor moieties via introducing substituent at the electron donor (anilino moiety) and/or acceptor (benzoyl moiety). This was based on the well-known linear correlation of the energy of the exciplex, E_{CT}, with the redox potentials of the electron donor (D) and acceptor (A) by the Weller eq 1,[10] which after introducing the ground-state repulsion energy, δE_{rep}, leads to eq 2 that correlates the emission energy of the CT state, $h\nu^{max}(CT)$, with the redox potentials.[11] This provides an alternative way of identifying the CT character of the emissive state by directly correlating the emission energy with the redox potentials of the electron donor/acceptor within the investigated fluorophores.

$$E_{CT} = E_D^{ox} - E_A^{red} - 0.15 \qquad (1)$$

$$h\nu^{max}(CT) = E_D^{ox} - E_A^{red} - \delta E_{rep} - 0.15 \qquad (2)$$

We therefore prepared a series of BA and MBA derivatives with substituents of different electron-withdrawing ability at the electron acceptor moiety (Scheme 1). Azumaya et al. [6] have reported a systematic investigation of ortho-substituted BA and MBA derivatives for the purpose of establishing the CT state conformation. To avoid the possible complexity caused by the ortho substitution, we only prepared the benzoyl para- and meta-substituted BA and MBA derivatives.

Although the measurement of the redox potentials of individual molecule is now an easy experiment, it turns to be not easy to measure the redox potentials for the electron donor and acceptor existing in the same molecule because of the possible difficulty in defining the electron donor/acceptor and choosing the model molecules for redox potentials measurements. As the Hammett substituent constant σ[12] is now easily available, we attempted to correlate the emission energy with σ, instead of the redox potentials, for establishing the CT character of the emissive state. This is theoretically likely. On the basis of the Weller equation, the free energy change of an electron-transfer reaction at the excited state in nonpolar solvent relates to the redox potentials of the electron donor and acceptor by formula 3[10,11]

$$\Delta G = E_D^{ox} - E_A^{red} - E_{0,0} + 0.38 \qquad (3)$$

in which $E_{0,0}$ is the energy of the locally excited state. In polar solvents, eq 3 still applies, but a stabilization energy term needs to be introduced in the right side. Combining eqs 2 and 3 leads to eq 4

$$h\nu^{max}(CT) = \Delta G + E_{0,0} - \delta E_{rep} - 0.53 \qquad (4)$$

which after incorporating the classic Hammett equation[13] establishes the relationship between the emission energy of the CT state and the substituent constant σ as given in eq 5

$$h\nu^{max}(CT) = -2.303RT\rho\sigma + E_{0,0} - \delta E_{rep} - 0.53 + C \quad (5)$$

in which ρ is the reaction constant defined in the classic Hammett equation, a positive ρ indicating that electron-withdrawing substituent enhances the involved reaction. R and T are gas constant and absolute temperature, respectively, and C is a constant equal to the emission energy of the parent molecule without substitution. It is thus obvious that a linear relationship between $h\nu^{max}(CT)$ and σ holds only in case that both $E_{0,0}$ and δE_{rep} or their difference remains constant in the series. In case of exciplexes formed from structurally related partners, δE_{rep} has been shown to be almost constant, which leads to the validity of eq 2 in many exciplex systems.[10,11] As in our case, the synthesized BAs and MBAs varied only in benzoyl substitution (Scheme 1), a constant δE_{rep}, and even $E_{0,0}$ might be expected.

The purpose of the present paper is to examine and compare the substituent effects on the emission of the BAs and MBAs, by correlating the emission energy with the Hammett substituent constant. It was hoped that by doing this it would be possible to provide new hints on the nature of the long-wavelength emissive states of BAs and MBAs and to estimate the extent of charge separation in case the CT character is identified. With all of the synthesized BA and MBA derivatives (Scheme 1), we observed dual fluorescence in cyclohexane. We found that, whereas the short-wavelength emission was hardly affected by the substitution, the long-wavelength emission energy indeed correlated linearly with the Hammett susbstituent constant in BA and MBA series, respectively, with almost the same linear slope, which provided direct evidence for the CT nature of the emissive state.

2. Experimental Section

Benzoyl-substituted benzanilides and *N*-methylbenzanilides (BAs and MBAs, Scheme 1) were synthesized by the reaction in the presence of anhydrous Na_2CO_3 in diethyl ether of aniline and *N*-methylaniline with substituted benzoyl chlorides that were in situ prepared from substituted benzoic acids and $SOCl_2$. The BAs and MBAs were purified by repeated recrystallization from acetone and were characterized by IR (Nicolet Avatar FT-IR 360) and ^1H NMR data (Varian Unity$^+$ 500 MHz, $CDCl_3$, TMS internal standard). Cyclohexane and diethyl ether used for absorption and fluorescence spectra measurements were purified just before use and were checked to have no fluorescent impurity at the employed excitation wavelength.

Corrected fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrometer with excitation wavelength of 280 nm 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 used. Quantum yields were measured using quinine sulfate (0.546 in 1N H_2SO_4 [14]) as a standard. The absorption spectra were taken on a Beckman DU-7400 spectrophotometer coupled with 1 cm quartz cell. All spectra were measured at a concentration of ca. 10^{-5} mol L^{-1} at room temperature (300 K).

TABLE 1: AM1 Optimized Ground-State Structural Parameters of BAs and MBAs

	BAs			MBAs		
	dihedral angles (°)[a]			dihedral angles (°)[a]		
R_1	C1−N−C1′−C2′	C3−C2 −C1−N	dipole moment (D)	C1−N−C1′−C2′	C3−C2 −C1−N	dipole moment (D)
p-OC_2H_5	6.7	41.2	3.52	41.7	51.8	3.11
p-CH_3	6.6	43.1	3.75	46.0	51.4	3.59
H	6.9	43.9	3.45	47.7	51.8	3.44
p-F	8.2	43.2	2.64	44.7	53.8	3.24
p-Cl	7.8	43.9	2.74	46.1	53.9	3.25
p-Br	7.8	44.4	2.69	48.1	54.4	3.28
m-Cl	7.8	44.0	2.54	50.1	52.9	3.99
m-NO_2	6.8	41.2	3.16	47.4	65.8	3.88
p-NO_2	9.0	46.2	4.30	50.3	59.8	5.40

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

The reduction potentials (vs. SCE) of the BAs were measured by cyclic voltammetry on BAS 200 electrochemical analyzer (BAS, U.S.) in a three-electrode configuration with a glass-carbon disk as the working electrode, SCE as the reference electrode, and a platinum wire as the counter electrode. The CV diagrams in ethanol−water (1:1, v/v) solution were taken under N_2 by scan rate of 0.1 V s^{-1} over the potential range of +1.0 to −3.0 V. A solution of 0.25 mol L^{-1} $(n\text{-}C_4H_9)_4NBr$ was used as the supporting electrolyte.

Ground-state geometrical structures were optimized by semiempirical AM1 method using MOPAC (version 97.0) programs in the Alchemy 2000 software package,[15] and the single-point calculations were performed by ab initio Hartree−Fock method using STO-3G basis sets in the Gaussian 94 program,[16] denoted as HF/STO-3G//AM1.

3. Results and Discussion

It was expected that by synthesizing only the para- and meta-substituted BAs and MBAs it would be possible to introduce mainly electronic polar effect while avoiding steric affect. To evaluate the steric impact of the substitution on the structures of BAs and MBAs, we carried out quantum mechanical calculations. The single-point calculations of the energies revealed that *cis*-BAs were ca. 3 kcal mol^{-1} higher in total energy than *trans*-BAs, whereas *cis*-MBAs were ca. 1 kcal mol^{-1} lower than *trans*-MBAs. This means that BAs exist preferentially in the trans conformation, whereas MBAs exist in the cis conformation, which is in agreement with previous reports[7a,17] on the conformational analysis of the parent BA and MBA without substituent. The dihedral angels and the ground-state dipole moments of the BA and MBA series were then calculated by the AM1 method. The results were summarized in Table 1. It was found from Table 1 that the benzoyl substitution indeed did not result in obvious change in the ground-state structures.

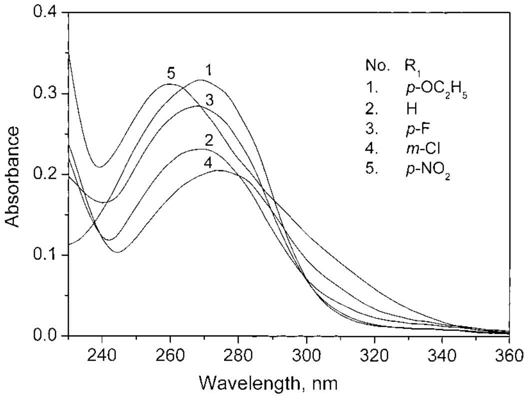


Figure 1. Absorption spectra of several BA derivatives in cyclohexane.

TABLE 2: Maximum Absorption Wavelengths of BAs and MBAs and Molar Absorption Coefficients in Cyclohexane

	BAs		MBAs	
R_1	λ_{max} (nm)	ϵ (mol^{-1} L cm^{-1})	λ_{max} (nm)	ϵ (mol^{-1} L cm^{-1})
p-OC_2H_5	270	18264	240/269	116331/11251
p-CH_3	269	21968	234/264	24424/8670
H	269	16024	250	11818
p-F	266	14495	250	10059
p-Cl	275	10467	239/268	28058/4486
p-Br	275	11919	237/265	22740/10808
m-Cl	274	13449	251	10602
m-NO_2	259	12040	253	16742
p-NO_2	259	11064	254	15832

The absorption spectra of BAs and MBAs in cyclohexane were recorded. Figure 1 illustrates, as examples, the absorption spectra of several BA derivatives. The absorption spectra of BAs showed a band around 270 nm with a tail extending to the range of 320 nm, and those of MBAs peaked around 240 nm with a shoulder at ca. 270 nm (Figure 1 and Table 2), which were similar to those of the parent BA and MBA reported previously in methylcyclohexane.[2−5,7] It was found that, in general, the absorption spectra of both BAs and MBAs showed very weak and no systematic dependence on the substitution (Table 2). The measured molar absorption coefficients of BAs and MBAs were found all at the order of the magnitude of 10^4 L mol^{-1} cm^{-1} (Table 2), suggesting that the main absorption band was due to the allowed (π, π^*) transition, as assigned for the parent BA and MBA.[3a,7a] The sluggish dependence of the absorption spectra on the substitution could be a reflection of the minor variation in the ground-state structure, as also indicated by the AM1 calculations shown in Table 1.

The fluorescence spectra of BAs and MBAs in cyclohexane were measured. Part of the spectra was given in Figure 2. We found that all of the synthesized BA and MBA derivatives, similar to the parent BA and MBA,[2−6] emitted dual fluorescence, with a short-wavelength band at around 330 nm and a long-wavelength band at the 500 nm region. The short-wavelength emission, previously assigned to the locally excited (LE) state,[2−6] was found to be very weak but showed practically no variation from each other of different substitutions (Figure 2). As both the absorption spectra and the LE emission of BAs and MBAs showed weak dependence on the substitution, it could be assumed that the $E_{0,0}$'s of BAs and MBAs remained more or less the same, respectively. Therefore, a linear relationship might be expected between the long-wavelength emission energy and the substituent constant with both BA and MBA series, if the emissive states are indeed of CT character.

We observed that, in clear difference from absorption and the short-wavelength LE emission, the long-wavelength emission of BAs and MBAs changed dramatically with the substitution (Figure 2 and Table 3). It was found that, with the same substituent, the maximum wavelength of the long-wavelength emission of the member in MBA series was longer than that in the BA series, and with both series, this wavelength strongly shifted to the red when the benzoyl substituent became increasingly electron demanding.

We found that the long-wavelength emission energies indeed correlated linearly with the Hammett substituent constants[13] in both BA and MBA series, with very close linear slopes of

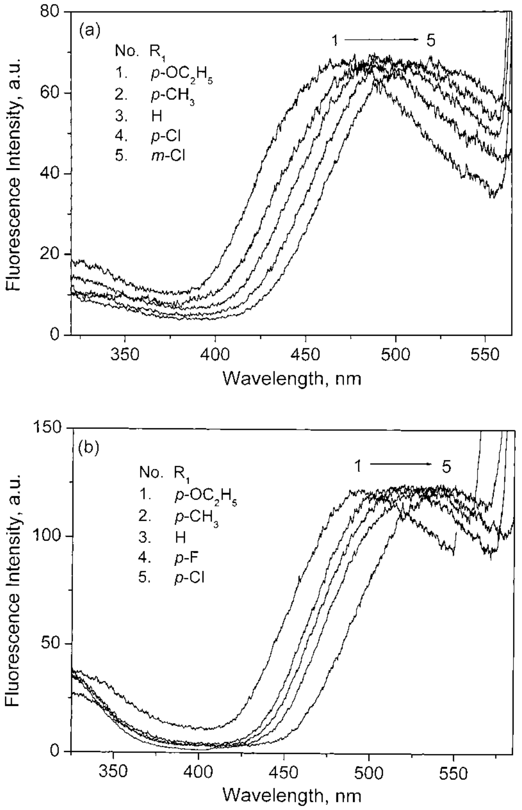


Figure 2. Fluorescence spectra of part of BAs (a) and MBAs (b) in cyclohexane.

TABLE 3: Maximum Wavelengths of the Long-Wavelength Emission, Quantum Yields of BAs and MBAs, and the Reduction Potentials of BAs Measured versus SCE

	BAs			MBAs		
	cyclohexane		DEE	cyclohexane		
R_1	λ_{max}(CT), nm	quant. yield	λ_{max}(CT), nm	λ_{max}(CT), nm	quant. yield	E_A^{red}, V (BAs)
p-OC_2H_5	470	0.0014	520	494	0.0034	−2.276
p-CH_3	483	0.0016	536	514	0.0027	−2.188
H	490	0.0019	545	530	0.0028	−2.179
p-F	481	0.0017	542	522	0.0029	*b*
p-Cl	504	0.0015	566	545	0.0021	−1.983
p-Br	505	0.0018	568	544	0.0020	−2.081
m-Cl	512	0.0014	576	555	0.0017	−1.973
m-NO_2	540	0.0003	*a*	580	0.0007	*b*
p-NO_2	546	0.0004	*a*	583	0.0004	*b*

[a] Not detected. [b] Not obtained.

−0.345 eV ($\gamma = 0.9811$, $n = 9$) for BAs and −0.343 eV ($\gamma = 0.9749$, $n = 9$) for MBAs (Figure 3). This linear relationship clearly pointed to the CT character of the long-wavelength emissive states of BAs and MBAs. The ρ values were calculated based on eq 5, as 5.80 for the BA series and 5.77 for the MBA series, respectively, which indicated that an electron-withdrawing substituent enhanced the reaction and, together with structural consideration, that the benzoyl moiety that bears the substituent was the electron acceptor in the CT reaction of BAs and MBAs. This is in agreement with the assignment of the electron donor and acceptor within BA and MBA.[3c,3d] It should be pointed out that, despite the possibility for PT reaction with the BAs, no PT could occur with the MBAs. The fact that similar slopes were found for both BA and MBA series (Figure 3) would hence mean that the same emissive state, i.e., the CT state, should be assumed for the long-wavelength emission of both BA and MBA series.

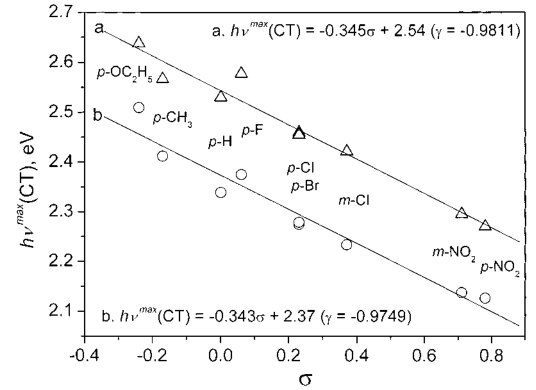


Figure 3. Linear correlation between the emission energies in cyclohexane of BAs (a) and MBAs (b) and the Hammett substituent constant σ.

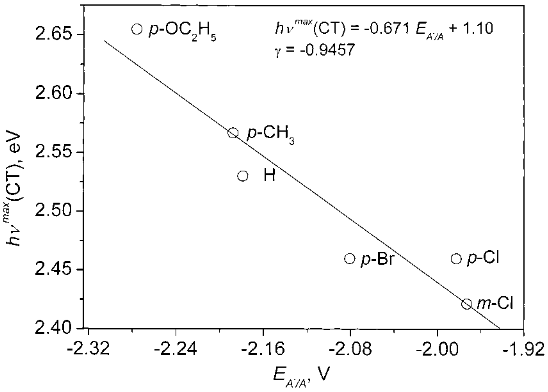


Figure 4. Plots of the emission energies of BAs in cyclohexane against the reduction potentials.

To estimate the charge separation extent in the CT state, we further measured the fluorescence spectra of BAs in a polar solvent, diethyl ether (DEE). Similar to the observation made in the nonpolar solvent cyclohexane, dual fluorescence was also observed in DEE, but the long-wavelength emission was shifted to the red for each molecule (Table 3), which is in agreement with the assignment of the CT emission. Plotting the emission energy of the long-wavelength fluorescence against the substituent constant σ, we again found a linear correlation in DEE, and importantly, the linear slope of −0.361 eV ($\gamma = 0.9723$, $n = 7$, intercept 2.28 eV) was close to that of −0.345 eV obtained in cyclohexane (Figure 2). As the increase in solvent polarity did not change very much the linear slope of the plot of $h\nu^{max}$(CT) against σ, it was concluded that a highly efficient charge transfer has occurred with BAs, and similarly with MBAs, as assumed in the original TICT state,[8] and the charges in the CT state are highly decoupled. This was supported by a direct correlation of the long-wavelength emission energies of BAs with their reduction potentials (Figure 4), which gave a linear slope (−0.671, $\gamma = 0.9723$, $n = 6$) close to −1 that is expected for the complete charge separation as observed with the exciplex (eqs 1 and 2).[10,11] It was therefore calculated that, for a full charge separation in the CT state, the slope for the linear relationship between $h\nu^{max}$(CT) and σ would be −0.5 or +0.5 eV for substituent at the electron acceptor and donor moiety, corresponding to ρ value of +8.5 and −8.5, respectively.

It should be pointed out that a similar linear relationship has been reported for the CT absorption.[18−20] At that time, however, the Hammett-like equation was written empirically.[19] It might be of interest to compare the ρ values reported previously with that obtained here. With the CT absorption of *N*-(X-benzyl)-pyridinium complexes[19] and X-phenylazoazulene[21] ρ ($\rho = -\rho_s$), values of 1.70 and −1.72 were reported,[19] whereas for the $E_T(30)$ dyes, the corresponding ρ values were around 3.[18,20] Obviously, the absolute values of these ρ's are substantially lower than that obtained here of 5.8. This might suggest a less efficient charge separation occurred with those previously reported systems.

Because of the highly decoupled character of the CT state, our results actually suggest a twisted CT configuration[6,7] around the amide C−N bond that connects the electron donor and acceptor in the BA and MBA series. Our AM1 calculations have shown that the BAs and MBAs had different preferential ground-state configurations (Table 1), whereas the weak dependence on the substitution of the absorption and the short-wavelength LE emission suggested a similar configuration of the LE state to that of the ground state. It hence followed that a configuration change occurred with the BAs and MBAs upon the excited-state CT reaction.

4. Conclusions

A series of para- and meta-substituted BAs and MBAs were synthesized, and all of the eighteen benzanilide and *N*-methylbenzanilide derivatives were found to emit dual fluorescence in the nonpolar solvent cyclohexane, with a normal emission at ca. 330 nm and a Stokes-shifted abnormal emission around 500 nm. Although the absorption and the short-wavelength emission showed weak dependence on the substitution, the long-wavelength emission strongly shifted to the red with increasing electron-withdrawing ability of the substituent. We theoretically showed that for the CT emission a linear correlation existed between the emission energy and the Hammett substituent constant and experimentally found that this was indeed the case for both BA and MBA series in cyclohexane and for BAs in DEE. This is the direct evidence for the CT nature of the long-wavelength emissive state for both BAs and MBAs. The observation of the linear slopes in three correlations were all close to −0.35 eV indicated that the long-wavelength emission of both BAs and MBAs was due solely to the CT state of the high extent of charge separation. This was supported by a linear correlation with a slope of −0.67 between the long-wavelength emission energies of BAs in cyclohexane and the reduction potentials. We concluded that the CT state of BAs and MBAs was of twisted configuration and a configuration change occurred upon the CT reaction. It was assumed that in case of a full charge transfer the slope of the linear correlation between $h\nu^{\max}(\text{CT})$ and σ would be −0.5 or +0.5 eV with the substituent at the electron acceptor and donor moieties, corresponding to ρ value of +8.5 and −8.5, respectively. The present report is, to the best of our knowledge, the first report that employs systematic molecular substitutions to show the direct spectroscopic evidence for the charge-transfer nature of the long-wavelength emission from BA and MBA.

Acknowledgment. This work has been supported by the National Natural Science Foundation (Grant Nos. 29975023 and 20175020) and by the Ministry of Education (MOE) of China.

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