Photochemical &
Photobiological Sciences

Cite this: *Photochem. Photobiol. Sci.*, 2011, **10**, 1791

www.rsc.org/pps

PAPER

Solvent-dependent intramolecular charge transfer dual fluorescence of *p*-dimethylaminobenzanilide bearing steric *ortho*,*ortho*-dimethyl substituents at amido aniline

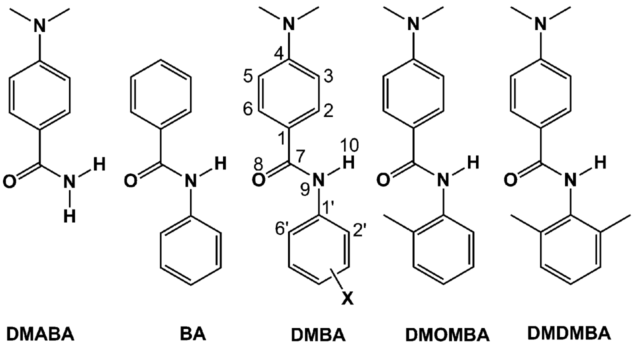
Xuan Zhang*[a] and Yun-Bao Jiang*[b]

Received 30th June 2011, Accepted 5th August 2011
DOI: 10.1039/c1pp05208j

Intramolecular charge transfer (ICT) dual fluorescence was observed in various organic solvents with *p*-dimethylaminobenzanilide (DMBA) derivatives bearing *ortho*-methyl (DMOMBA) and *ortho*,*ortho*-dimethyl (DMDMBA) substituents at amido aniline moiety. *Ab initio* calculation and absorption spectral data indicated that high steric hindrance was introduced by the *ortho*,*ortho*-dimethyl substitutions. It was found that, with DMDMBA, the CT emission initially shifted to the red with increasing solvent polarity from cyclohexane (CHX, 480 nm) to diethyl ether (DEE, 520 nm), similar to those of DMBA derivatives with the *ortho*-, *meta*- or *para*-methyl substitutions at amido aniline moiety. However, there is a characteristic blue-shift of the long wavelength emission between DEE and tetrahydrofuran (THF, 424 nm) then a bathochromic shift again in highly polar solvent acetonitrile (ACN, 484 nm). The unusual solvent-dependent CT emission was ascribed to two competitive CT channels. One is benzanilide (BA)-like CT, whose CT reaction occurs from amido aniline to benzoyl moiety in nonpolar solvent CHX and DEE; the other one is *p*-dimethylaminobenzamide (DMABA)-like, whose CT reaction occurs from dimethylamino to benzanilide moiety in highly polar solvent THF and ACN. These findings revealed the steric effect plays an important role in the ICT process, which may alter the properties of the electron donor and/or acceptor, but also change the reaction potential.

1. Introduction

Intramolecular charge transfer (ICT) dual fluorescence of *p*-dimethylaminobenzonitrile (DMABN) and related derivatives has drawn much experimental and theoretical attention.[1–12] Both the electronic and steric factors were considered to be important for the occurrence of the charge transfer reaction.[2,3] Rettig *et al.*[13] have examined the electronic factors of the electron acceptor on the CT emission of *p*-dimethylaminobenzamide (DMABA, Scheme 1) by diminishing the electron-acceptor character, by varying the amide group from $-C(O)NH_2$ through $-C(O)N(CH_3)_2$ to $-C(O)N(C_2H_5)_2$. Although a systematic blue shift of the CT emission and the decrease of the emission intensity ratio between CT and locally excited (LE) states were observed, it was found that a considerable steric effect was also introduced at the amide moiety that may also contribute to the change of CT emission.[13] Recently, we employed an alternative strategy that successfully showed the important role that the electronic factor of the electron donor/acceptor played in the CT process.[14–18] In these investigations, the possible steric effect was avoided by introducing substitution only at the *para*- or *meta*-position of the phenol moieties in the phenyl *p*-dimethylaminobenzoates,[14] or the amido aniline moieties in *p*-dimethylaminobenzanilides (DMBA, X = H, Scheme 1),[17] to modify the electron donor/acceptor. The *ortho*-substituent effect on CT process, however, remained unclear and requires some further investigation.



Scheme 1 Molecular structures of investigated compounds. X in DMBA are H, *p*-CH_3 and *m*-CH_3, respectively. The numbers were used to define the dihedral angle.

---

[a] *College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, 201620, China. E-mail: xzhang@dhu.edu.cn*
[b] *Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen, 361005, China. E-mail: ybjiang@xmu.edu.cn*

Table 1 Dihedral angles, bond lengths and dipole moments in the ground state[a]

	Dihedral angles, °[b]				Bond lengths, Å		
Compounds	θ_1	θ_2	θ_3	θ_4	C(O)–N	C(Ph)–N	Dipole moment, D
DMBA							
X = H	1.3	2.3	20.1	17.4	1.372	1.419	5.39
X = *p*-CH_3	1.3	2.5	20.2	17.5	1.370	1.420	5.38
X = *m*-CH_3	1.6	2.1	20.1	17.5	1.371	1.419	5.14
DMOMBA	0.0	2.5	19.6	16.0	1.393	1.423	5.82
DMDMBA	58.9	42.8	20.6	18.5	1.395	1.437	5.50

[a] Calculated using Gaussian 98[24] and the molecular structures are shown in Scheme 1. [b] Dihedral angels defined in Scheme 1, θ_1, ∠C6′–C1′–N9–C7; θ_2, ∠C2′–C1′–N9–H10; θ_3, ∠C2–C1–C7–N9 and θ_4, ∠C6–C1–C7–O8.

With DMBA (X = H, Scheme 1), a compound combining the competitive CT reactions of both DMABA[13] and benzanilide (BA),[15–22] it was found that, with increasing the electron-withdrawing ability of the *para*- or *meta*-substituent to the amido anilino moiety, the CT reaction initially occurred from the amido aniline moiety to the rest of the molecule (BA-like), and tended to occur from dimethylamino group to benzanilide moiety (DMABA-like).[17] The peculiar CT character of DMBA derivatives prompted us to select it as a model system to further examine the *ortho*-methyl substitution effect on the CT reaction.

We report herein a description of the steady-state absorption and fluorescence spectra of DMBA derivatives with *ortho*-methyl and *ortho*,*ortho*-dimethyl substitutions to the amido anilino moiety (DMOMBA and DMDMBA, Scheme 1). Comparison of *ab initio* calculations and absorption spectral data indicates that the *ortho*,*ortho*-dimethyl substitution introduces a significant steric change in the structure of DMDMBA derivative, and as a consequence the CT fluorescence was found to be solvent dependent, which was BA-like in nonpolar solvents such as cyclohexane (CHX) and diethyl ether (DEE), but DMABA-like in polar solvents such as tetrahydrofuran (THF) and acetonitrile (ACN). The reason of the influence of the steric hindrance on the solvent-dependent CT emission behavior is discussed in the paper.

2. Materials and methods

DMOMBA and DMDMBA were synthesized by heating *p*-dimethylaminobenzoic acid and the corresponding substituted aniline in the presence of $POCl_3$ as described previously.[17]

4-Dimethylamino-2′-methylbenzanilide (DMOMBA). IR (KBr, cm^{-1}), 3294, 3047, 2919, 1631, 1604. ^1H NMR (500 MHz, DMSO-d_6), δ (ppm) 2.22 (s, 3H), 2.99 (s, 6H), 6.75 (d, 2H, $J = 9$ Hz), 7.13 (m, 1H), 7.19 (m, 1H), 7.24 (d, 1H, $J = 7$ Hz), 7.32 (d, 1H, 9 Hz), 7.86 (d, 2H, 9 Hz), 9.47 (s, 1H).

4-Dimethylamino-2′,6′-dimethylbenzanilide (DMDMBA). IR (KBr, cm^{-1}), 3288, 3037, 2920, 1631, 1609. ^1H NMR (500 MHz, DMSO-d_6), δ (ppm) 2.16 (s, 6H), 2.99 (s, 6H), 6.76 (d, 2H, $J = 8.5$ Hz), 7.10 (s, 3H), 7.88 (d, 2H, $J = 9$ Hz), 9.38 (s, 1H).

IR data were taken on a Nicolet FT-IR 360 spectrophotometer with a KBr pellet and ^1H NMR data were acquired in DMSO-d_6 on a Varian Unity$^+$ 500 MHz NMR spectrometer using TMS as the internal standard. The absorption spectra were recorded on Varian Cary 300 spectrophotometer coupled with a 1 cm quartz cuvette. Corrected fluorescence spectra were taken on a Hitachi F-4500 fluorescence spectrophotometer using excitation and emission slits of 5 nm. The excitation wavelength was 305 nm. Fluorescence quantum yields (Φ_F) were measured using quinine sulfate as a standard (0.546 in 1 N H_2SO_4).[23] *Ab initio* calculations at Hartree–Fock (HF) self-consistent field level were carried out using Gaussian 98.[24] Solvents for spectroscopic investigations were purified before use and checked to have no fluorescent impurity at the used excitation wavelength. All spectra were measured at sample concentrations of *ca.* 10^{-5} M.

3. Results and discussion

3.1 Optimized geometry of DMBA derivatives

To evaluate the measure of steric hindrance introduced by the *ortho*-methyl substitutions at amido anilino moiety, *ab initio* calculations were performed on DMOMBA and DMDMBA (Scheme 1) and parts of the structure parameters were presented in Table 1, in which the corresponding values of DMBA and its *para*- or *meta*-methyl substituted derivatives were also listed for comparison. As noted from Table 1, the ground state conformations of DMBA and its *para*- or *meta*-methyl substituted derivatives, as well as DMOMBA were almost planar ($\theta_1 < 2°$, $\theta_2 < 3°$), whereas DMDMBA was very twisted at the amido aniline moiety ($\theta_1 = 58.9°$, $\theta_2 = 42.8°$), even the amide benzoyl dihedral angles θ_3 and θ_4 were almost the same in all of the DMBA derivatives (Scheme 1). While the slight variation was found in the ground state dipole moment, both the bond lengths of amide C(O)–N and C(Ph)–N bonds of DMDMBA were obviously longer than those of other DMBA derivatives investigated (Table 1). Therefore, it is reasonable to conclude that in the case of DMDMBA, the *ortho*,*ortho*-dimethyl substitution introduces a large increase in the angle of plane of the amido anilino moiety compared with the plane of the DMBA subgroup, as it is otherwise expected.

3.2 Absorption spectra of DMBA derivatives

Fig. 1 showed the absorption spectra of DMBA, DMOMBA, DMDMBA and DMABA in cyclohexane (CHX) and acetonitrile (ACN). The absorption spectra of DMOMBA in CHX were found to be only slightly shifted to the blue by *ca.* 3 nm than that of DMBA.[17] With DMDMBA, however, the absorption spectra were significantly blue-shifted (*ca.* 12 nm) and more similar to that of DMABA (Fig. 1a), revealing that high steric hindrance was indeed introduced by *ortho*,*ortho*-dimethyl substitution.[25,26] In all cases, an obvious shoulder can be seen at *ca.* 300 nm, which is scarcely affected by substitution and readily ascribed

Table 2 Spectroscopic data for DMOMBA and DMDMBA in organic solvents

			Absorption		Fluorescence	
Compounds	Solvent[a]	f–f'[b]	λ_{max}, nm	ε, 10^4 M^{-1} cm^{-1}	$\lambda_{LE}/\lambda_{CT}$, nm	Φ_F
DMOMBA	CHX	0.000	304	2.50	343/460	0.0011
	DEE	0.161	302	2.54	346/508	0.0070
	THF	0.208	305	2.54	354/518	0.0043
	ACN	0.306	309	2.39	370/498	0.0059
DMDMBA	CHX	0.000	295	2.89	336/480	0.0015
	DEE	0.161	293	2.86	344/520	0.0036
	THF	0.208	296	3.47	352/424	0.0059
	ACN	0.306	302	3.34	364/484	0.0158

[a] Solvent: CHX, cyclohexane; DEE, diethyl ether; THF, tetrahydrofuran; and ACN, acetonitrile. [b] Taken from ref. 27.

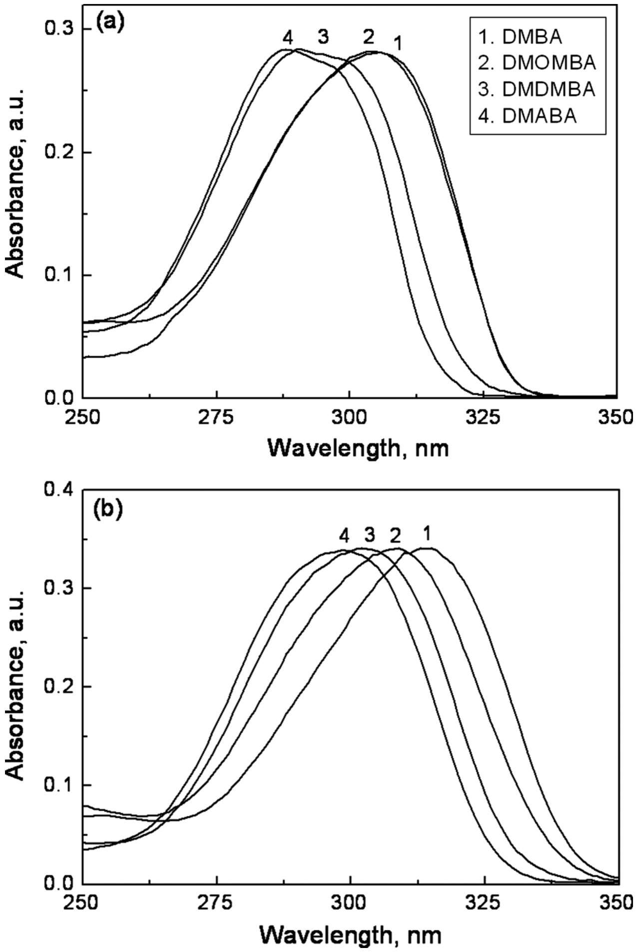


Fig. 1 Normalized absorption spectra of investigated compounds (Scheme 1) in CHX, cyclohexane (a) and ACN, acetonitrile (b).

to ^1L_b state transition, while the main absorption assigned to ^1L_a state transition that is sensitive to the substitution as observed previously in donor–acceptor-substituted aniline derivatives.[13] In the highly polar solvent ACN, the absorption spectra of all DMBA derivatives only slightly shifted to the red than those in CHX, reflecting the small dipole moment of the ground state, meanwhile the absorption bands were well separated with different substitution (Fig. 1b and Table 2). It has been shown that *para*- and *meta*-methyl substitution at the amido anilino moiety scarcely affected the absorption spectrum of DMBA, in which only the substituent electronic effect was considered to be involved.[17] We could therefore conclude that the steric hindrance introduced by *ortho*,*ortho*-dimethyl substitution of DMDMBA, affects the energy of the electronic transitions, in good agreement with the *ab initio* calculations (Table 1).

3.3 Fluorescence spectra of DMBA derivatives

The fluorescence spectra of DMOMBA and DMDMBA were presented in Fig. 2. From CHX to DEE, the dual fluorescence was observed for DMOMBA and DMDMBA, which is very similar to those of the *para*- or *meta*-methyl substituted DMBA derivatives.[17] With increasing solvent polarity from CHX to DEE, while the short-wavelength emission underwent a minor variation, the long-wavelength fluorescence remarkably shifted to the red (Fig. 2 and Table 2), indicating the charge transfer nature of the emissive state. The dual fluorescence was hence readily attributed to the LE and CT states, respectively. As suggested for other DMBA derivatives,[17] the CT reaction probably occurs from amido aniline to benzoyl moiety (BA-like).[15–22] However, the CT emission of DMDMBA shows a surprising blue-shift in THF (a solvent of medium polarity) compared with the less polar DEE, but it shifted to the red again in highly polar solvent ACN (Fig. 2a and Table 2). This could be explained as BA-like CT reaction mixing with the DMABA-like CT reaction, since it is known that in the same solvent the DMABA-like CT emission locates at a shorter wavelength than the BA-like CT emission.[15,17]

To trace the detailed change of solvent-dependent CT emission, the fluorescence spectra of DMDMBA were recorded in DEE-ACN binary solvents and the normalized emission spectra are shown in Fig. 3. With increasing solvent polarity by increasing the ACN portion in the binary solvents, it could be observed clearly that the BA-like CT emission around 530 nm was quenched, but a new emission gradually emerged at shorter wavelength (*ca.* 430 nm) and red-shifted strongly, which indicates the CT nature of the new emissive state. Comparing the CT emission behavior of DMDMBA with those of DMOMBA and *para*- or *meta*-methyl substituted DMBA derivatives (Scheme 1), the fluorescence of DMDMBA in THF and ACN can be readily ascribed to the DMABA-like CT emission.[17] This was supported by the fact that the emission behavior of DMDMBA in ACN was very similar to that of DMABA in the same solvent (Fig. 2b).[13]

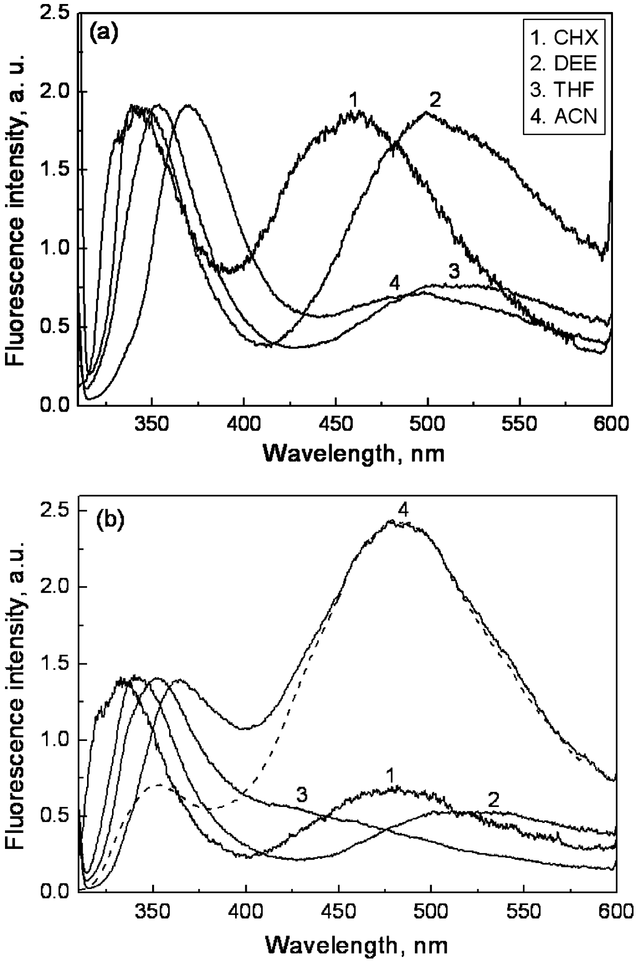


Fig. 2 Fluorescence spectra normalized at LE emission of DMOMBA (a) and DMDMBA (b) in various organic solvents. CHX, cyclohexane; DEE, diethyl ether; THF, tetrahydrofuran; and ACN, acetonitrile. The fluorescence spectra of DMABA in ACN (dashed line) are presented in Fig. 2b for comparison.

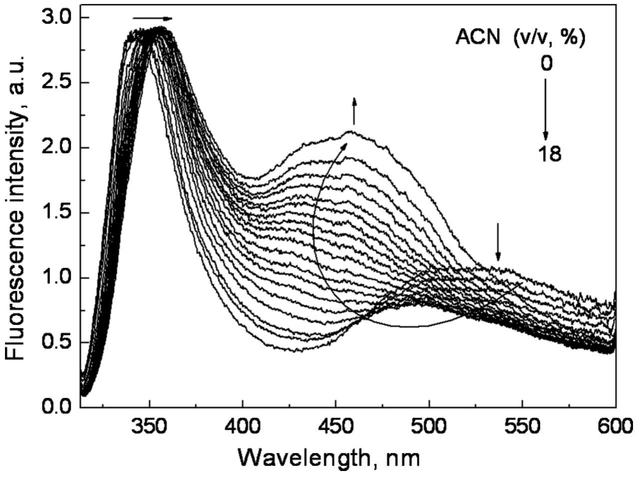


Fig. 3 Fluorescence spectra normalized at LE emission of DMDMBA in DEE with increasing the compositions of ACN from 0 to 18% with interval 1%.

3.4 Solvent-dependent ICT dual fluorescence of DMDMBA

Fig. 4 shows the variations of the CT to LE intensity ratio and CT emission energy of DMBA and its *para*-, *meta*-, *ortho*-methyl and *ortho*,*ortho*-dimethyl substituted derivatives with solvent polarity indexed by *f*-*f′*.[27] It can be noted that the ratios of CT to LE intensities of DMBA and its *para*- and *meta*-methyl substituted derivatives initially increased with increasing solvent polarity (from CHX to DEE), then decreased with further increasing polarity through THF to ACN (Fig. 4). Even the similar variation profile was observed in *ortho*-methyl substituted DMOMBA, however, a very different profile was found in highly steric *ortho*,*ortho*-dimethyl DMDMBA (Fig. 4), where the ratio of CT to LE intensity showed a slight decrease from CHX through DEE to THF, but a sharp increase in ACN. In addition, the variation of CT emission energy of DMDMBA also clearly shows a different profile from those of DMBA and its *para*-, *meta*- and *ortho*-methyl substituted derivatives (Fig. 4), where a sharp blue-shift was observed in THF in DMDMBA. These results reveal the solvent-dependent competitive CT emission of DMDMBA, namely, in the nonpolar solvents CHX and DEE the CT emission is BA-like, whose CT occurred from the amido aniline moiety to the benzoyl moiety,[15–22] however, in polar solvents THF and ACN the CT emission is the DMABA-like, in which the dimethylamino group is the electron donor and the rest of molecule is the electron acceptor.[13,17] It should be also noted that the CT fluorescence emission of DMOMBA in ACN appears at a similar wavelength region with that of DMDMBA, however, the intensity ratio of CT to LE is much smaller than that in the case of highly steric DMDMBA. This is at good agreement with the enhancement CT reaction by *ortho*,*ortho*-dimethyl substitution as observed by Rettig *et al.*,[25,26] reflecting the important role of steric effect played in the CT reaction.

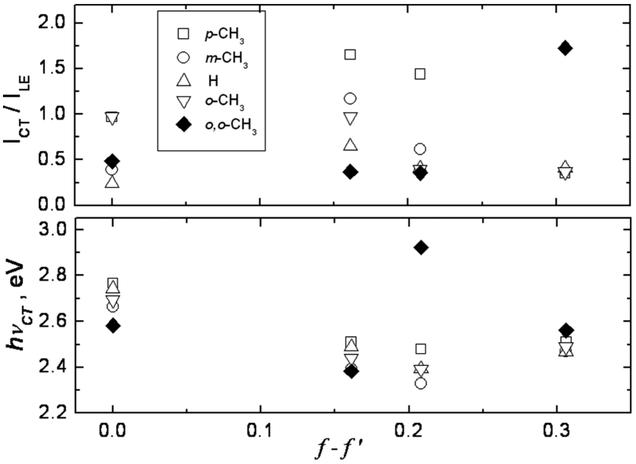
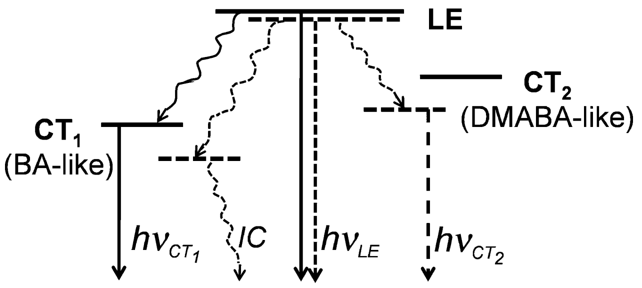


Fig. 4 Variations of the CT to LE emission intensity ratio (up) and CT emission energy (bottom) of DMBAs with different substitutions at the amido aniline moiety in CHX, cyclohexane; DEE, diethyl ether; THF, tetrahydrofuran; and ACN, acetonitrile.

The unusual solvent dependence of ICT fluorescence of dual emission behavior can be illustrated by the help of Scheme 2. The DMDMBA molecule at the LE state (**LE**, Scheme 2) could return to its ground state by emitting LE fluorescence $h\nu_{LE}$ from **LE**, BA-like ($h\nu_{CT1}$) and DMABA-like ($h\nu_{CT2}$) CT fluorescence



Scheme 2 Illustration of solvent-dependent CT dual fluorescence of DMDMBA in nonpolar solvent CHX (solid line) and polar solvent ACN (dashed line).

from CT states (**CT$_1$** and **CT$_2$**, Scheme 2). In the nonpolar solvent CHX, besides LE fluorescence emission, **CT$_1$** can be populated *via* internal conversion (*IC*) process due to very low energy barrier between the **LE** and **CT$_1$**, but high energy barrier between the **LE** and **CT$_2$** does not allow efficient population of the **CT$_2$**, so that only the BA-like CT fluorescence was observed. In the case of polar solvent ACN, while the **LE** was slightly stabilized and emits somewhat red-shifted LE fluorescence, both **CT$_1$** and **CT$_2$** were stabilized much more effectively, and even more importantly the energy barrier between **LE** and **CT$_2$** was considerably decreased with increasing solvent polarity.[28] Consequently, both the **CT$_1$** and **CT$_2$** can be populated *via* the *IC* process from **LE**, however, while the strong DMABA-like CT fluorescence emission was observed, the BA-like CT fluorescence was seriously quenched due to the large stabilization of **CT$_1$** efficiently enhanced the *IC* process between **CT$_1$** and ground state. The fluorescence quantum yield of DMDMBA (0.0156) is smaller than that of DMABA (0.020)[13] in ACN, which is in agreement with the existence of the additional BA-like CT deactivation channel in DMDMBA, where an *IC* process from **CT$_2$** to **CT$_1$** might also be possible. The more efficient *IC* process between **CT$_1$** and ground state in DMDMBA could be readily understood from its lower energy **CT$_1$** state, which was revealed by longer BA-like CT fluorescence emission in DMDMBA (480 nm) than those of the *para*-, *meta*- and *ortho*-methyl substituted DMBA derivatives (465 nm, 452 nm and 460 nm, respectively) in CHX. These findings show that the steric hindrance effect plays an important role in the CT reaction that may alter the property of electron donor and/or acceptor, but possibly also change the CT reaction potential.

4. Conclusions

The *ortho*-methyl and *ortho*,*ortho*-dimethyl substituted DMBA derivatives, DMOMBA and DMDMBA, were synthesized to examine the steric hindrance effect on the CT reaction. While the absorption spectra of DMOMBA only underwent a slightly blue-shift, a drastic blue-shift was observed for that of DMDMBA, implying that the high steric hindrance was introduced by *ortho*,*ortho*-dimethyl substitutions, which was in good agreement with the ground state *ab initio* calculations. The dual fluorescence, from the LE and CT states, was observed with DMOMBA and DMDMBA from nonpolar solvent CHX to polar solvent ACN. In CHX, the CT fluorescence of DMOMBA and DMDMBA was ascribed to the BA-like emission, where the CT reaction occurred from amido aniline to benzoyl moiety. In ACN, the CT fluorescence of DMDMBA was found to be different from those of *para*-, *meta*- and *ortho*-methyl substituted DMBA derivatives, and ascribed to the DMABA-like emission, where the CT reaction occurred from the dimethylamino group to the benzanilide moiety. The solvent-dependent CT fluorescence emission behavior of DMDMBA was explained by consideration of, with increasing solvent polarity, both a drastic decrease of energy barrier from LE to DMABA-like CT state and an efficient enhancement of internal conversion process from BA-like CT state to ground state. These findings reveal a steric hindrance effect can play an important role in the CT reaction that may alter the property of electron donor and/or acceptor, but possibly also change the activation energies of the excited state reactions. These types of examinations could be helpful for a deeper understanding of the photophysical behavior of DMABA and BA, as well as other compounds with competitive CT channels, which may also contribute in the future to design of novel balance-like ICT dual fluorescent probes.[29]

Acknowledgements

We thank Dr C.-J. Wang for geometry calculation. This work was supported by the National Natural Science Foundation of China through grants No. 20175020 and The Fundamental Research Funds for the Central Universities (DHU-2011D10511).

Notes and references

1 Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley and W. Baumann, Twisted intramolecular charge transfer states (TICT). A new class of excited states with a full charge separation, *Nouv. J. Chim.*, 1979, **3**, 443–454.
2 W. Rettig, Charge separation in excited states of decoupled systems-TICT compounds and implications regarding the development of new laser dyes and the primary processes of vision and photosynthesis, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 971–988.
3 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, Structural changes accompanying intramolecular electron transfer. Focus on twisted intramolecular charge-transfer states and structures, *Chem. Rev.*, 2003, **103**, 3899–4032.
4 W. Schuddeboom, S. A. Jonker, J. M. Warman, U. Leinhos, W. Kühnle and K. A. Zachariasse, Excited-state dipole moments of dual fluorescent 4-(dialkylamino)- benzonitriles. Influence of alkyl chain length and effective solvent polarity, *J. Phys. Chem. A*, 1992, **96**, 10809–10819.
5 K. A. Zachariasse, Th. von der Haar, A. Hebecker, U. Leinhos and W. Kühnle, Intramolecular charge transfer in aminobenzonitriles: requirements for dual fluorescence, *Pure Appl. Chem.*, 1993, **65**, 1745–1750.
6 K. A. Zachariasse, M. Grobys, T. von der Haar, A. Hebecker, Y. V. Il'ichev, O. Morawski, I. Rückert and W. Kühnle, Photoinduced intramolecular charge transfer and internal conversion in molecules with a small energy gap between S1 and S2. Dynamics and structure, *J. Photochem. Photobiol., A*, 1997, **105**, 373–383.
7 Yu. V. Il'ichev, W. Kühnle and K. A. Zachariasse, Intramolecular charge transfer in dual fluorescent 4-(dialkylamino)benzonitriles. Reaction efficiency enhancement by increasing the size of the amino and benzonitrile subunits by alkyl substituents, *J. Phys. Chem. A*, 1998, **102**, 5670–5680.
8 W. Fuß, K. K. Pushpa, W. Rettig, W. E. Schmid and S. A. Trushin, Ultrafast charge transfer *via* a conical intersection in dimethylaminobenzonitrile, *Photochem. Photobiol. Sci.*, 2002, **1**, 255–262.
9 C. J. Jödicke and H. P. Lüthi, Time-dependent density-functional theory (TDDFT) study of the excited state charge transfer state formation of a series of aromatic donor–acceptor systems, *J. Am. Chem. Soc.*, 2003, **125**, 252–264.
10 S. I. Druzhinin, S. A. Kovalenko, T. A. Senyushkina, A. Demeter and K. A. Zachariasse, Intramolecular Charge Transfer with Fluorazene and N-Phenylpyrrole, *J. Phys. Chem. A*, 2010, **114**, 1621–1632.

11 J. Sung, P. Kim, Y. Lee, J. S. Kim and D. Kim, Characterization of ultrafast intramolecular charge transfer dynamics in pyrenyl derivatives: Systematic change of the number of peripheral N,N-dimethyaniline substituents, *J. Phys. Chem. Lett.*, 2011, **2**, 818–823.

12 N. Dash and G. Krishnamoorthy, Modulation of the photophysics of 2-(4′-N,N-dimethylaminophenyl)imidazo-[4,5-b]pyridine by long chain N-alkylations, *Photochem. Photobiol. Sci.*, 2011, **10**, 939–946.

13 D. Braun, W. Rettig, S. Delmond, J. F. Létard and R. Lapouyade, Amide derivatives of DMABN: A new class of dual fluorescent compounds, *J. Phys. Chem. A*, 1997, **101**, 6836–6841.

14 W. Huang, X. Zhang, L.-H. Ma, C.-J. Wang and Y.-B. Jiang, Intramolecular charge transfer dual fluorescence of substituted-phenyl p-dimethylaminobenzoates with comparable electron acceptors, *Chem. Phys. Lett.*, 2002, **352**, 401–407.

15 X. Zhang, X.-Y. Sun, C.-J. Wang and Y.-B. Jiang, Substituent effect on the dual fluorescence of benzanilides and N-methylbenzanilides in cyclohexane. Direct evidence for intramolecular charge transfer, *J. Phys. Chem. A*, 2002, **106**, 5577–5581.

16 X. Zhang, L.-H. Ma, X.-Y. Sun, C.-J. Wang, Z. Li, F.-Y. Wu and Y.-B. Jiang, Dual flrorescence of anilino substituted benzanilides in non-polar solvent cyclohexane -Direct spectroscopic evidence for the excited-state charge transfer, *Chem. J. Chin. Univ.*, 2002, **23**, 1701–1703.

17 X. Zhang, C.-J. Wang, L.-H. Liu and Y.-B. Jiang, Reversal of the intramolecular charge transfer in p-dimethylaminobenzanilides by amido anilino substitution, *J. Phys. Chem. B*, 2002, **106**, 12432–12440.

18 X. Zhang, C.-H. Liu, L.-H. Liu, F.-Y. Wu, L. Guo, X.-Y. Sun, C.-J. Wang and Y.-B. Jiang, Intramolecular charge transfer with N-benzoylaminonaphthalenes. 1-Aminonaphthalene *versus* 2-aminonaphthalene as electron donors, *Org. Biomol. Chem.*, 2003, **1**, 728–732.

19 I. Azumaya, H. Kagechika, Y. Fujiwara, M. Itoh, K. Yamaguchi and K. Shudo, Twisted intramolecular charge-transfer fluorescence of aromatic amides: conformation of the amide bonds in the excited states, *J. Am. Chem. Soc.*, 1991, **113**, 2833–2838.

20 F. D. Lewis and T. M. Long, Anomalous dual fluorescence of benzanilide, *J. Phys. Chem. A*, 1998, **102**, 5327–5332.

21 F. D. Lewis and W.-Z. Liu, Temperature- and conformation-dependent luminescence of benzanilides, *J. Phys. Chem. A*, 2002, **106**, 1976–1984.

22 F. D. Lewis, T. M. Long, C. L. Stern and W.-Z. Liu, Structures and excited states of extended and folded mono-, di-, and tri-N-arylbenzamides, *J. Phys. Chem. A*, 2003, **107**, 3254–3262.

23 J. N. Demas and G. A. Crosby, The measurement of photoluminescence quantum yields. A review, *J. Phys. Chem.*, 1971, **75**, 991–1024.

24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian Inc., Pittsburgh, PA, 1998.

25 S. Kapelle, W. Rettig and R. Lapouyade, Dual fluorescent polyaniline model compounds: steric and temperature effects on excited state charge separation, *Photochem. Photobiol. Sci.*, 2002, **1**, 492–499.

26 S. Kapelle, W. Rettig and R. Lapouyade, Aniline dimers and trimers as model compounds for polyaniline: steric control of charge separation properties, *Chem. Phys. Lett.*, 2001, **348**, 416–424.

27 K. A. Zachariasse, M. Grobys and E. Tauer, Absence of dual fluorescence with 4-(dimethylamino)phenylacetylene. A comparison between experimental results and theoretical predictions, *Chem. Phys. Lett.*, 1997, **274**, 372–382.

28 A. Demeter, S. Druzhinin, M. George, E. Haselbach, J. L. Roulin and K. A. Zachariasse, Dual fluorescence and fast intramolecular charge transfer with 4-(diisopropylamino)benzonitrile in alkane solvents, *Chem. Phys. Lett.*, 2000, **323**, 351–360.

29 L.-H. Liu, H. Zhang, A.-F. Li, J.-W. Xie and Y.-B. Jiang, Intramolecular charge transfer dual fluorescent sensors from 4-(dialkylamino)benzanilides with metal binding site within electron acceptor, *Tetrahedron*, 2006, **62**, 10441–10449.