

Intramolecular charge transfer dual fluorescence of substituted-phenyl *p*-dimethylaminobenzoates with comparable electron acceptors

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Abstract

A series of substituted-phenyl *p*-dimethylaminobenzoates with *para*- or *meta*-substitution at the ester phenyl ring (*p*-OH, *p*-CH₃, H, *p*-Br, *m*-Cl, and *p*-NO₂) were synthesized and their fluorescence spectra were recorded. Intramolecular charge transfer (CT) dual fluorescence was observed in polar solvents. The CT emission in the same solvent was found to shift to lower energy with increasing electron-withdrawing ability of the substituent, whereas the locally excited (LE) emission hardly showed any change. A linear correlation was found between the CT emission energies of the four of the six esters and the Hammett constants of the substituents in diethyl ether, tetrahydrofuran and ethyl acetate and the linear slopes were -0.190 , -0.169 and -0.138 eV, respectively, that decreased with increasing solvent polarity. The implications of the present findings were discussed in terms of structural relaxation during the excited-state CT reaction and of designing new fluorescence chemosensors. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

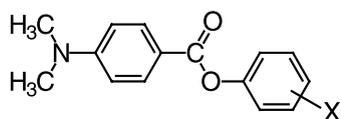
With the intramolecular charge transfer (CT) dual fluorescent *para*-substituted *N,N*-dialkylanilines, such as *p*-dimethylaminobenzonitrile (DMABN), the dialkylamino group has been considered to be the electron donor while the rest of the molecule to be the acceptor [1,2]. The investigations of the influence of electron donor and/or acceptor on the CT process have then been of great importance for the understanding of the CT

photophysics, in particular with regard to the CT dynamics and the structural relaxation upon the CT process. Such investigations, however, have been focused mainly on the influence of the electron donors [3–6], whereas those with the electron acceptors have been limited. The latter was recently examined by Rettig and coworkers on the dual fluorescent *N,N*-dimethylanilines with electron-withdrawing groups substituted at the *para*-position [7,8] and with *p*-dimethylaminobenzamides of different amido groups [9]. Different from the case with the variations in the electron donors, it has not been easy to have a set of CT dual fluorescent molecules with comparable electron acceptors. In the series of the electron-

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withdrawing groups ($-\text{CN}$, $-\text{CO}_2\text{CH}_3$, $-\text{CHO}$, $-\text{COCH}_3$, $-\text{CONH}_2$ [7,8,10], $-\text{CF}_3$ [11] and $-\text{SO}_3\text{Na}$ [12]) *para*-substituted *N,N*-dimethylanilines, the variations in the acceptors could also change the excited-state reaction coordinates, for instance, in the cases with cyano and carboxylate *para*-substituted *N,N*-dimethylanilines [2]. In the series of *p*-dimethylaminobenzamides [9] a steric effect was also introduced along with the electron polar effect when the amido moiety was changed from $-\text{CONH}_2$ through $-\text{CON}(\text{CH}_3)_2$ to $-\text{CON}(\text{C}_2\text{H}_5)_2$. In spite of these complexities the examination on the effect of the electron acceptor variations has indeed led to interesting observations that would be of great importance to the understanding of the CT photophysics [9]. We therefore attempted to construct a series of dual fluorescent *N,N*-dimethylaniline derivatives with *comparable* electron acceptors.

It has been shown that the $-\text{NH}-$ bridge could efficiently transmit the substituent effect [13,14]. Our first attempt was hence made to substituted-phenyl *p*-dimethylaminobenzoates (Scheme 1), hoping to achieve the variations of the electron-accepting ability of the acceptor moiety by substitution at the ester phenyl ring while the ester identity of the acceptor moiety remains unchanged. In these esters the phenoxy $-\text{O}-$ bridge was employed to transmit the substituent effect, since the $-\text{O}-$ bridge was expected to be similar to the $-\text{NH}-$ bridge while avoid the complicated $n-\pi^*$ transition in the amide derivatives [9]. In order to avoid the possible steric effect due to the *ortho*-substitution only the *para*- and *meta*-substitutions were tried. The AM1 calculations pointed out that no appreciable steric effect was introduced in our series of substituted-phenyl *p*-dimethylaminobenzoates (Scheme 1). Fluorescence spectra recorded in polar solvents indicated



X = *p*-OH (1), *p*-CH₃(2), H(3), *p*-Br(4), *m*-Cl(5), *p*-NO₂(6)

Scheme 1. Molecular structure of substituted-phenyl *p*-dimethylaminobenzoates.

that CT occurred with these esters. In this Letter we will report the electron-acceptor dependence in the CT dual fluorescence and its implications to the structural relaxation upon CT reaction and the CT dual fluorescence chemosensor designing.

2. Experimental

Substituted-phenyl *p*-dimethylaminobenzoates (Scheme 1) were synthesized by reaction of *p*-dimethylaminobenzoic acid with substituted phenols in the presence of POCl_3 . The products were repeatedly recrystallized and characterized by IR and NMR data. Organic solvents were purified before use and were checked to have no fluorescent impurity at the used excitation wavelength.

Corrected fluorescence spectra and the absorption spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer and Beckman DU-7400 absorption spectrophotometer, respectively. Quantum yields of the aerated sample solutions were measured using quinine sulfate as the standard (0.546 in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ [15]). IR data of the KBr plated samples were acquired from Nicolet Avatar FT-IR 360 spectrometer and NMR data were taken on Varian Unity⁺ 500 MHz spectrometer (CDCl_3 , TMS). AM1 calculations were carried out using GAUSSIAN 94 software [16].

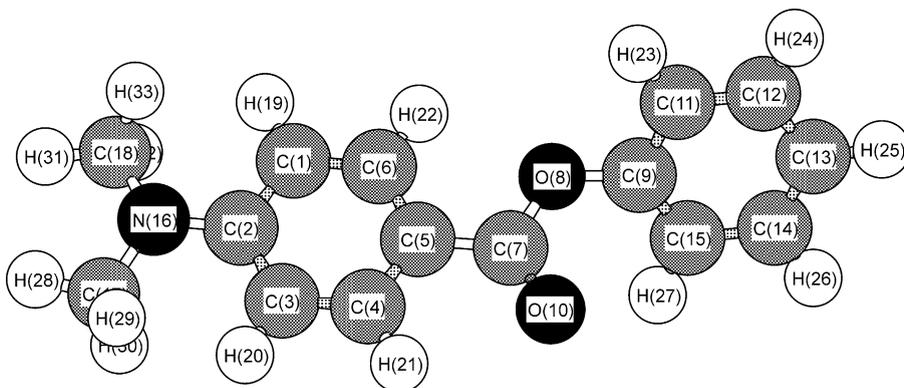
3. Results and discussion

We synthesized a series of substituted-phenyl *p*-dimethylaminobenzoates (Scheme 1) in which the electron acceptors were varied by introducing substituent at the *para*- or *meta*-position of the ester phenyl ring in order to avoid the steric effect while electronic polar effect was incorporated. We here called the ester phenyl ring the mediator that communicates via the phenoxy $-\text{O}-$ bridge the electronic polar effect of the substituent with the dimethylaminobenzoyl moiety of the molecule. We expected that by designing this series of molecules we could generate a series of the CT dual fluorescent esters with the same electron donor while varied but comparable electron acceptors.

The ground-state structures of the synthesized esters were optimized with the aid of the AM1 calculations. The optimized structure of phenyl *p*-dimethylaminobenzoate (**3**, Scheme 1), as an example, was shown in Scheme 2. The structural parameters of the synthesized esters are given in Table 1. It is obvious from Table 1 that, except the ester with *para*-nitro substituent, the ester conjunction moiety dihedral angles and the ground-state dipole moments of the other five esters did not vary very much. This means that, as expected, no appreciable steric effect has been introduced by the *para*- or *meta*-substitution, thereby ensuring the comparability of the electron acceptors in the synthesized esters. The higher ground-state dipole moment of *p*-nitrophenyl *p*-dimethylaminobenzoate (**6**, Scheme 1) might indicate the occurrence of the ground-state CT. This was also reflected in the

stretching vibration frequency of the carbonyl double bond in ester **6**, see Table 2. The observed stretching frequency of 1716 cm^{-1} for ester **6** was appreciably higher than those of the others that are $1711 \pm 1\text{ cm}^{-1}$ for esters **2–5** and 1705 cm^{-1} for ester **1** (Table 2). The deviation of the stretching frequency of carbonyl double bond in ester **1** with hydroxyl substituent could be the consequence of the intermolecular hydrogen bonding [17].

The absorption spectra in tetrahydrofuran (THF) were recorded (Fig. 1 and Table 2). It was found from Fig. 1 and Table 2 that the maximum absorption wavelength shifted slightly to the red with increasing electron-withdrawing ability of the substituent, with the exception of the hydroxyl substituted ester that might result from the intermolecular hydrogen bonding. The absorption of



Scheme 2. AM1 optimized structure of phenyl *p*-dimethylaminobenzoate.

Table 1

AM1 calculated dihedral angles at the ester conjunction moieties and the ground-state dipole moments, together with the measured CT state dipole moments

| X | Dihedral angle (°) | | μ_g (D) | $\mu_c(\text{CT})$ (D) ^a |
|---------------------------|--------------------------|---------------------------|-------------|-------------------------------------|
| | C6–C5–C7–O8 ^b | C7–O8–C9–C15 ^b | | |
| <i>p</i> -OH | 0.3 | 51.3 | 4.39 | 13.80 |
| <i>p</i> -CH ₃ | 1.3 | 49.6 | 4.02 | 16.34 |
| H | 3.7 | 50.1 | 4.33 | 18.40 |
| <i>p</i> -Br | 1.2 | 46.4 | 5.98 | 15.09 |
| <i>m</i> -Cl | 0.9 | 48.4 | 4.91 | 13.43 |
| <i>p</i> -NO ₂ | 3.8 | 42.4 | 10.45 | – |

^a Measured from solvatochromic data, see details in the text.

^b The atom numbers were indicated in Scheme 2.

Table 2

The IR stretching frequencies of the carbonyl double bonds and the absorption and fluorescence spectral parameters of the substituted-phenyl *p*-dimethylaminobenzoates in THF

| X | $\nu_{\text{C=O}}$ (IR, cm^{-1}) | $\lambda_{\text{abs}}^{\text{max}}$ (nm) | ϵ^{max} ($\text{mol}^{-1} \text{ l cm}^{-1}$) | $\lambda_{\text{LE}}/\lambda_{\text{CT}}$ (nm) | Total quantum yield |
|---------------------------|---|---|--|---|---------------------|
| <i>p</i> -OH | 1705 | 319 | 1.86×10^4 | 358/476 | 0.024 |
| <i>p</i> -CH ₃ | 1712 | 315 | 2.23×10^4 | 359/470 | 0.052 |
| H | 1710 | 316 | 2.14×10^4 | 352/475 | 0.027 |
| <i>p</i> -Br | 1710 | 319 | 3.37×10^4 | 355/484 | 0.019 |
| <i>m</i> -Cl | 1713 | 319 | 2.58×10^4 | 352/486 | 0.019 |
| <i>p</i> -NO ₂ | 1716 | 323 | 1.50×10^4 | 350/504 | 0.0072 |

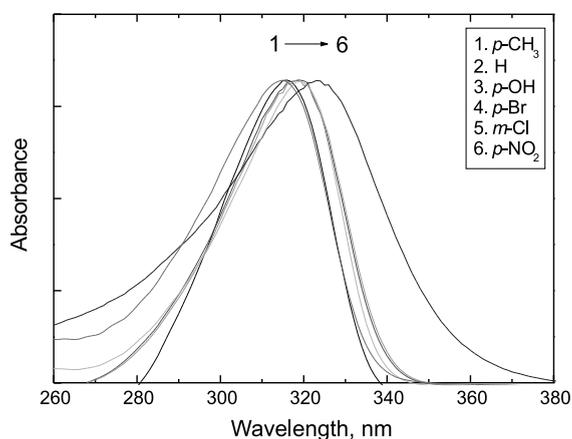


Fig. 1. Absorption spectra of the substituted-phenyl *p*-dimethylaminobenzoates in THF.

the ester **6** with *para*-nitro substitution was found to be obviously broader at the long-wavelength side (Fig. 1) and to have lower molar absorption coefficient than those of the others (Table 2), supporting the previous assumption of the ground-state CT. Because of the complexity with the *para*-hydroxyl and *para*-nitro substituted esters (**1** and **6**, Scheme 1), the following correlation will only include the data of the other four esters (**2–5**) that we showed with comparable electron acceptors.

The fluorescence spectra were recorded in solvents of different polarity. Fig. 2 shows as examples the emission spectra of phenyl *p*-dimethylaminobenzoate (**3**, Scheme 1). The emission spectra of the other esters showed similar variations with solvent polarity. It was found that, like the aliphatic alkyl *p*-dimethylaminobenzoates

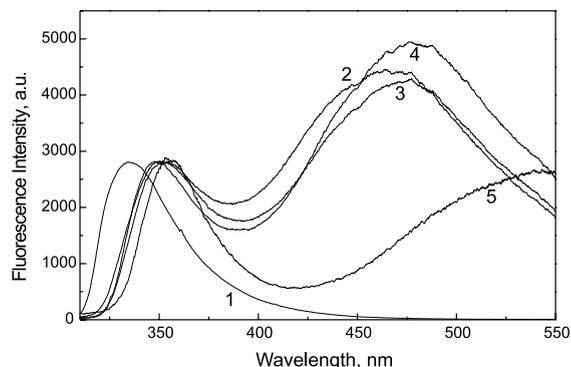


Fig. 2. Fluorescence spectra of phenyl *p*-dimethylaminobenzoate in solvents of varied polarity. Solvents are cyclohexane (CH, 1), diethyl ether (DEE, 2), tetrahydrofuran (THF, 3), ethyl acetate (EtOAc, 4) and acetonitrile (ACN, 5), respectively.

[2], substituted-phenyl *p*-dimethylaminobenzoates emitted dual fluorescence in polar solvents. In non-polar solvent cyclohexane the esters emitted mainly the short-wavelength fluorescence, with tail extending to beyond 450 nm. The clearly observed dual fluorescence in polar solvents could be readily assigned to the locally excited (LE) state and the charge transfer (CT) state, respectively, as done with the alkyl *p*-dimethylaminobenzoate [2]. In agreement with the previously reported observations, the LE emission of the substituted-phenyl *p*-dimethylaminobenzoates at around 355 nm showed very weak dependence on solvent polarity, whereas a substantial dependence was observed with the CT emission that allowed for the measurement of the dipole moments of the CT state. The CT state dipole moments were estimated from

the solvatochromic data following a reported method [18] by plotting the CT emission energies against those of DMABN in corresponding solvents. The ground and the CT state dipole moments of DMABN of 6.6 and 17 D, respectively, were taken [18], and the equivalent spherical radius of the solute was calculated by assuming a density of 1. The results were given in Table 1. No systematic variation in the CT state dipole moments of the substituted-phenyl *p*-dimethylaminobenzoates was found, which means that the CT state dipole moment practically does not change with the substitution.

The CT emissions of the substituted-phenyl *p*-dimethylaminobenzoates were compared in several solvents of different polarity. Fig. 3 displays the fluorescence spectra of esters in diethyl ether and

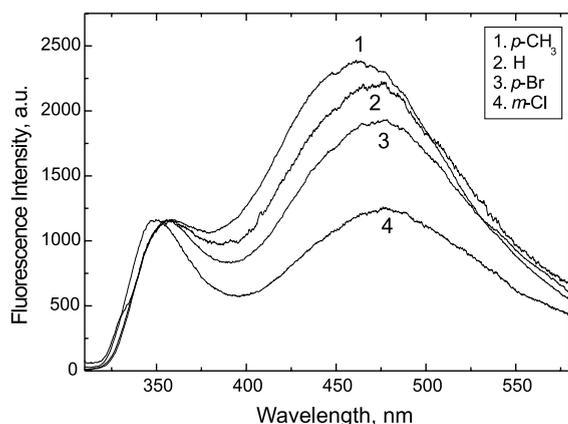


Fig. 3. Dual fluorescence emission of the substituted-phenyl *p*-dimethylaminobenzoates in diethyl ether. The substituents at the ester phenyl ring are *p*-CH₃ (1), H (2), *p*-Br (3) and *m*-Cl (4), respectively.

the CT emission data in several other solvents were given in Table 3. It was found that the CT emission shifted to the red when the substituent at the phenyl ring became more electron demanding and the CT emission energy correlated linearly with the Hammett substituent constant σ , see Fig. 4. The absolute linear slope was shown to decrease with increasing solvent polarity. The LE emission that emitted from the non-CT state, however, showed hardly any dependence on the substituent constant in these solvents and in non-polar solvent cyclohexane in which the LE emission wavelength could be accurately measured.

It should be pointed out that correlation of the electron-transfer parameters to the redox potentials of electron donor and acceptor has been a well-accepted strategy for intermolecular electron transfer [20,21]. Problems, however, could arise with the intramolecular CT reaction since the defining of the identities of electron donor and acceptor and the choosing of their model molecules for redox potential measurements are not straightforward. We therefore attempted to extend the correlation to the Hammett substituent constant with the intramolecular CT in substituted-phenyl *p*-dimethylaminobenzoates. Indeed, we showed that, by combining the Weller equations on the exciplex energy and the free energy change of the excited-state electron transfer [20,21], together with the classic Hammett equation [22], the CT emission energy correlated linearly with the Hammett substituent constant as given in Eq. (1), provided the LE state energy, $E_{0,0}$, and the repulsion energy of the Franck–Condon ground-state reached after the CT emission, δE_{rep} , or their difference remain constant within the molecule series

Table 3

The CT emission wavelengths of the substituted-phenyl *p*-dimethylaminobenzoates in DEE, THF and ethyl acetate together with the Hammett substituent constants

| X | σ^a | $\lambda^{\text{max}}(\text{CT})$ (nm) | | |
|---------------------------|------------|--|-----|-------|
| | | DEE | THF | EtOAc |
| <i>p</i> -CH ₃ | -0.17 | 461 | 470 | 476 |
| H | 0 | 465 | 475 | 477 |
| <i>p</i> -Br | 0.23 | 475 | 484 | 484 |
| <i>m</i> -Cl | 0.37 | 477 | 486 | 490 |

^a Taken from [19].

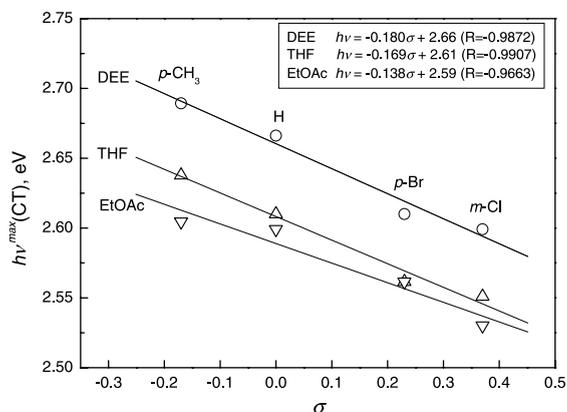


Fig. 4. The linear dependences of the CT emission energies on the Hammett substituent constants in DEE, THF and ethyl acetate. The linear correlation equations together with correlation coefficients are included in the figure.

$$h\nu^{\max}(\text{CT}) = -2.303RT\rho\sigma + E_{0,0} - \delta E_{\text{rep}} - 0.53 + C. \quad (1)$$

We have shown that the absorption spectra and the LE emission wavelengths of the esters **2–5** that were included in the correlation were more or less the same (Table 2 and Fig. 3), the $E_{0,0}$ values can be reasonably assumed to be the same. The similar ground-state structure and CT state dipole moment (Table 1) would support the assumption that δE_{rep} does not vary very much within these four esters. The observation of the linear dependence of the CT emission energies with the Hammett substituent constants (Fig. 4) was actually a reflection of these facts. The linear slopes in DEE, THF and ethyl acetate (EtOAc) were -0.190 , -0.169 and -0.138 eV, corresponding to ρ values at 298 K of 3.05, 2.86 and 2.34, respectively. This observation confirms that the $-\text{O}-$ bridge, like the $-\text{NH}-$ bridge [13,14], could indeed transmit the substituent effect. The positive reaction constant ρ indicates that an electron-demanding substituent promotes the CT reaction in the excited state, suggesting that the substitution at the ester phenyl ring could indeed modify the strength of the electron acceptor in a comparable manner.

The linear dependence shown in Fig. 4 would be of use for constructing CT dual fluorescence chemosensors based on the modification of the

electron-acceptor strength, while the solvent polarity effect on this dependence suggested that a less polar (micro)environment should be offered for the CT fluorophore to ensure the strongest response to the variations in the electron-acceptor strength. The fact that the linear dependence shown in Fig. 4 becomes weaker in more polar solvent in which the CT process is favored indicates that in more polar solvent the $-\text{O}-$ bridge becomes less efficient in transmitting the substituent effect, which would mean that the communication is increasingly blocked. This in turn points to the occurrence of a structural relaxation around the $-\text{O}-$ bridge during the CT reaction. With *p*-dimethylaminobenzamides it was suggested that a structural relaxation might occur around the amido nitrogen atom [9].

4. Conclusions

A series of six substituted-phenyl *p*-dimethylaminobenzoates were prepared and the AM1 calculations and absorption and IR data suggested that the ground-state structures were hardly changed in most of the esters. The CT dual fluorescence was observed with all of the six esters in polar solvents and the CT emission was found to be shifted to the red when the substituent at the ester phenyl ring became increasingly electron demanding, from *p*- CH_3 via H and *p*-Br to *m*-Cl, while with all the six esters the LE emission showed hardly any variation. A linear dependence was found between the CT emission energies and the Hammett substituent constants in DEE, THF and ethyl acetate and the linear dependence became weaker with increasing solvent polarity. Such dependence did not exist with the series of the dual fluorescent *N,N*-dimethylanilines with electron-withdrawing substituents at the *para*-position [2,7–9]. Our observation of this linear dependence offers a new hint for constructing CT dual fluorescence chemosensors based on modification of the electron-acceptor strength, while the solvent polarity effect on this dependence instructs the choosing of medium a less polar environment should be provided for the CT fluorophore. The solvent polarity effect on the linear dependence also pointed to the

occurrence of the structural relaxation around the phenoxyl –O– bridge during the CT process. We showed that with phenyl *p*-dimethylaminobenzoates substitution at the phenyl ring could indeed generate a series of dual fluorescent CT fluorophores with varied but comparable electron acceptors.

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