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Study on photophysical properties of intramolecular charge transfer (ICT) compound: 4-(diphenylamino)biphenyl-4′-boronic acid

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Abstract

A new compound 4-(diphenylamino) biphenyl-4′-boronic acid (DBBA) was synthesized. The optical properties including fluorescence quantum yields and change in the dipole moment in various solvents at room temperature were characterized by the absorption and steady-state fluorescence technique. The emission wavelength of DBBA was very sensitive to the polarity of solvents. The magnitude of change in the dipole moment was calculated based on the Lippert–Mataga equation. DBBA has an increase of dipole moment of 4.9 D units on excitation to the lowest singlet state. A high fluorescence quantum yields (ϕ_f) and short fluorescence decay times (τ_f) were determined in all solvents tested. The bathochromic shift of the emission spectra and the increase in the excited state dipole moment occurred. These gave the evidence about the intramolecular charge transfer (ICT) character in the emitting singlet state of DBBA.

Keywords: Intramolecular charge transfer; Fluorescence; Dipole moment

1. Introduction

Intramolecular charge transfer (ICT) has always been attracting considerable attention as a topic of central importance both in photochemistry and in biochemistry [1–7]. The excited state electron transfer in organic donor–acceptor (D–A) compounds is usually described in terms of electronic coupling between the locally excited (LE) state and the charge transfer (CT) state [8]. This process will lead to a large increase of the dipole moment, and hence will cause a marked solvatochromic effect and a large Stokes shift. Therefore, recently the organic donor–acceptor (D–A) compounds, whose fluorescent spectra are sensitive to the change in the solvent properties, have been increasing interest and usually been used as the fluorescent probe to study microenvironments [9–13], e.g. the polarity and viscosity change in micelle, microemulsion, vesicle and liposome. Nowadays the electron transfer and charge transfer processes in various donor–acceptor system upon excitation [14,15] were characterized.

Triphenylamine and its derivatives are very promising functional molecular materials. They have attacted much attention because they are not only important organic dyes but also can act as one of photoinduced charge transfer layers in electrophotography and electroluminescence [16]. Therefore, the study on their photophysical properties is significant for a better understanding of the process of photoinduced charge transfer and the practical applications. The photophysics properties of some triphenylamine derivatives, such as diphenyl amino-substituted triphenylbenzene (PEFTP), biphenyl (PEFBP) and fluorine (PEFF) derivatives [17,18], hexadecyl 4-biphenylaminobenzoate (HBAB)[19], 4-formacyl-triphenylamine (FTA) and 4,4′-bisformacyl-triphenylamine (BTA) [16] have been reported. These triphenylamine derivatives with donor (amino group) and acceptor (a strong acceptor group) moieties in one

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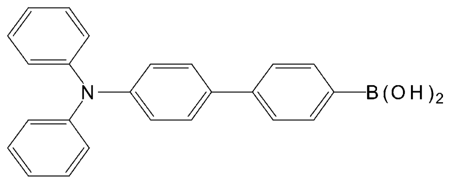

Fig. 1. The molecular structure of compound DBBA.

molecule are strong polar molecule whose emission is mainly ICT or TICT emission. This kind of compounds may potentially serve as functional materials of organic molecular electronics, such as fluorescence probe, photo-charge exchanging materials and so on. However, these triphenylamine derivatives are limited to the compounds containing a strong electron acceptor group, such as formacyl, ester group. So it is necessary to study some triiphenylamine derivatives with a weak acceptor group in the molecule.

4-(Diphenylamino) biphenyl-4′-boronic acid (DBBA) (Fig. 1) is of triphenylamine's derivatives with a weak acceptor group of boron group. It was synthesized firstly. In the present paper, we intend to explain the particular behavior of compound DBBA by means of UV and fluorescence spectra measurements in a variety of nonpolar and polar solvents at room temperature, and by an approximate determination of increasing dipole moment on excitation to the lowest singlet state, fluorescence quantum yields and fluorescence decay times.

2. Experimental

DBBA was synthesized in our lab following a procedure described in the literature [20] and was confirmed by ^{1}H NMR, ^{13}C NMR and MS spectroscopy. The solvents, cyclohexane, ethylether, acetone, tetrahydrofuran, ethylacetate, acetonitrile, ethanol and methanol were all purchased from Beijing Chemical Plant without further purification prior to use. No interference fluorescence was observed under the experimental conditions for all the reagents used.

The absorption spectra were recorded on a UV-265 spectrophotometer (Shimadzu) and corrected emission spectra were obtained on a F-4500 spectrofluorometer (Hitachi). Excitation and emission bandwidths were both set at 2.5 nm. The fluorescence decay times were measured with PTI fluorescence lifetime scanning spectrometer, and the excitation wavelength was at 337 nm. All experiments were performed at 20 ± 1 °C.

3. Results and discussions

3.1. Absorption and fluorescence spectra

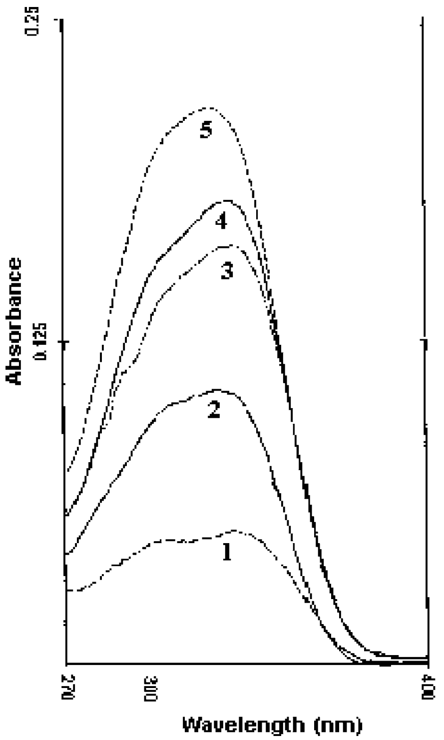

Fig. 2. The absorption spectra of DBBA in various solvents (1) cyclohexane, (2) ethylether, (3) tetrahydrofuran, (4) ethanol, and (5) methanol.

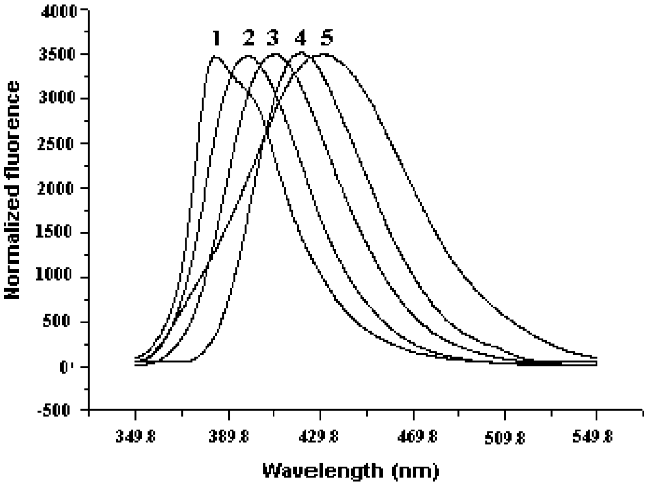

Fig. 3. Normalized fluorescence spectra of DBBA in various solvents (1) cyclohexane, (2) ethylether, (3) tetrahydrofuran, (4) ethanol, and (5) methanol.

Fig. 2 showed the absorption spectra of DBBA in various solvents including cyclohexane, ethylether, tetrahydrofuran, ethanol and methanol. The maxima of absoprption spectra were slightly shifted from 333 to 326 nm, which was probably due to the decrease of the solvent refractive index from cyclohexane to methanol. The normalized fluorescence spectra of DBBA were shown in Fig. 3. It was noted that the fluorescence spectra were independent of the exciting wavelength. The presence of a single emission band indicated a barrierless electron transfer process. The maximum emission wavelength was red-shift from 384 to 398, 410, 422 and 432 nm, respectively in the presence of different solvents. The about

Table 1
Maximum wavelength of absorption and fluorescence and Stokes shift for compound DBBA in the solvents studied

Solvent	Δf[a]	$E_T(30)$[b] (kcal/mol)	$\Delta\nu_{1/2}$ (cm^{-1})	λ_a (nm)	ν_a (cm^{-1})	λ_f (nm)	ν_f (cm^{-1})	$\Delta\nu_{Stoke}$ (cm^{-1})
Cyclohexane	0.101	31.2	3171	332.8	30048	384.0	26042	4006
Ethylether	0.257	34.6	3466	330.0	30303	398.0	25126	5177
Tetrahydrofuran	0.309	37.4	3681	331.0	30211	410.0	24390	5821
Ethanol	0.379	51.9	4213	329.6	30340	422.4	23674	6666
Methanol	0.393	55.5	4965	326.0	30675	432.0	23148	7527

See text for details of column titles.

[a] Polarity function for each solvent is based on the value of dielectric constant and refractive index of the solvents given in Ref. [21].

[b] Values taken from Ref. [22].

50 nm of maximum shift was observed. Moreover, the fluorescence halfwidth $\Delta\nu_{1/2}$ increased from 3171 to 4965 cm^{-1}. This polar stable ICT state may exist in polar solvents and make the DBBA molecule relaxation to the equilibrium geometry of the electronic state. As a result, the fluorescence spectra show a red-shift and the halfwidth of the fluorescence band become broad.

The corresponding spectral characteristics in a variety of solvents with different polarity were detailed listed in Table 1. As can be seen in Table 1 and Figs. 1 and 2, the polarity of the solvent has a larger effect on the emission band maxima (λ_f) of DBBA than on the absorption band maxima (λ_a). This observation indicates that photoinduced intramolecular charge transfer (ICT) takes place within the molecule in the singlet-excited state in comparison with the ground state. The increase of the Stokes shift about 3521 cm^{-1} with increasing the solvent polarity suggests that the potential energy surface of the emitting state is considerably different from that of the ground state and has a charge transfer character of the fluorescence states, i.e. a large increase in the excited state dipole moment.

3.2. *Measurement of the magnitude of the change in the dipole moment*

Fig. 4(a) showed the emission maxima (ν_f) of compound DBBA to the different solvent polarity parameter $E_T(30)$ value. Least square linear regression analysis gave a good correlation. This is commonly considered that it is the result of stabilizing the state of charge transfer by solvent molecule [23]. Determination of the extent of increase in the dipole moment of the dye on electronic excitation can be made from the Lippert–Mataga relation [24], in polar and in fairly polar solvents, the relation between the solvent-dependent shift of the emission maxima ν_f and the solvent parameter $\Delta f(\varepsilon, n)$ is expressed as follows:

$$\nu_f = \nu_{f0} - \frac{2\Delta u^2}{4\pi\varepsilon_0 hc\rho^3}\Delta f(\varepsilon, n) \qquad (1)$$

where $\Delta f(\varepsilon, n) = ((\varepsilon - 1)/2(\varepsilon + 1)) - ((n^2 - 1)/2(2n^2 + 1))$, ε, n corresponds to the static dielectric constant, the refractive index of the medium, ν_f and ν_{f0} the emission maxima(wavenumbers) in a solvent and in vacuum, $\Delta\mu = (\mu_e - \mu_g)$ the magnitude of the change in the dipole moment on excitation from the ground state to the excited state, h, c, ε_0, ρ corresponds to Plank's constant (6.6×10^{-34} JS), the velocity of light in vacuum (3.0×10^8 ms^{-1}), the permittivity of vacuum (8.85×10^{-12} VC^{-1} m^{-1}) and the Onsagar cavity radius (in meter). Using the assumption of Lippert that the Onsagar Cavity radius ρ can be derived from the length of the molecule (16.3 Å) multiplied by a reduction factor of 0.8 [25], gives the value 13.0 Å.

A plot of the emission maxima ν_f versus the polarity function $\Delta f(\varepsilon, n)$ was shown in Fig. 4(b). Least square linear regression analysis gave a good correlation according to

$$\nu_f = 27414 - 10680\Delta f(\varepsilon, n) \qquad (r = 0.95)$$

The emission maxima ν_f versus $\Delta f(\varepsilon, n)$ were linear and the slope was 10 680. According to Eq. (1) it approximately corresponded to a dipole moment of 4.9 D for the charge transfer state relative to the ground state. This was due to intramolecular charge transfer from amino group to boron group in the excited state of compound DBBA. This large change in dipole moment from ground to excited state was caused by the redistribution of atomic charges in excited state,

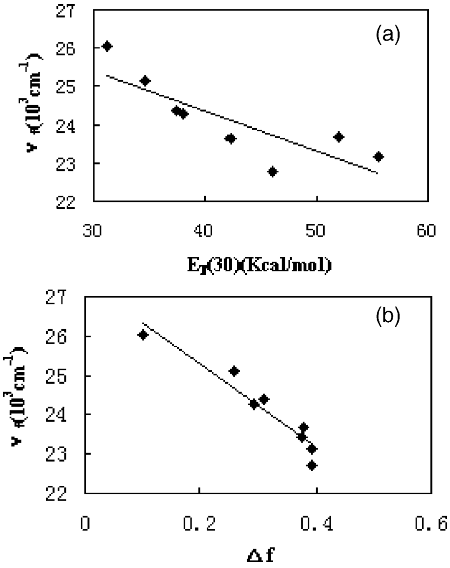

Fig. 4. (a) Dependence of emission maxima (ν_f) of DBBA on solvent polarity $E_T(30)$ value; (b) emission maxima (ν_f) as a function of the solvent polarity-polarizability parameter (Δf) for compound DBBA. Solvents are cyclohexane, ethylether, tetrahydrofuran, ethylacetate, acetone, acetonitrile, ethanol, methanol.

Table 2
Decay parameters of the excited singlet state of DBBA in different solvents

Solvents	ϕ_f	τ_f (ns)	k_f[a] ($\times 10^7$ s^{-1})	k_{nr}[b] ($\times 10^7$ s^{-1})	$k_f/n^2\nu^3$[c] (10^7 s^{-1} cm^{-3})
Cyclohexane	0.72	1.59	45.3	17.6	126
Ethylether	0.65	1.69	38.5	20.7	133
Tetrahydrofuran	0.65	2.14	30.4	16.4	106
Ethylacetate	0.66	2.21	29.9	15.4	111
Acetonitrile	0.68	2.24	30.4	14.3	146
Ethanol	0.81	2.39	33.9	7.9	138
Methanol	0.62	2.97	20.9	12.9	95

See text for details of column titles.

[a] Rate constant of fluorescence.

[b] Rate constant of nonradiative decay.

[c] $k_f/n^2\nu^3$ is proportion to the oscillator strength.

which was only possible due to charge transfer from election rich donor moiety to acceptor moiety. The high $\Delta\mu$ value of DBBA revealed a strong increase in the excited state dipole moment and confirming the CT character of the excited state.

3.3. *Fluorescence quantum yield and fluorescence decay time*

The fluorescence quantum yields were obtained using quinine bisulfate in 0.05 mol/l sulphuric acid as standard [26]. The values of ϕ_f for DBBA were obtained using the following relation [27]:

$$\phi_f^u = \phi_f^s \frac{F_u A_s n_u^2}{F_s A_u n_s^2} \tag{2}$$

where, F represents the corrected fluorescence peak area, A the absorbance at the excitation wavelength, n the refractive index of the solvent used, ϕ_f the fluorescence quantum efficiency and the subscripts “s” and “u” refer to standard and unknown, respectively.

According to Eq. (2), fluorescence quantum yields (ϕ_f) of DBBA in various solvents were shown in Table 2. Obviously fluorescence quantum yields (ϕ_f) of DBBA were found to be generally very high and almost constant in all solvents studied. The fluorescence decay curves were obtained by the single photon technique and a single-exponential equation. As were shown in Table 2, the fluorescence decay times became longer with the increase of polarity of the solvents. This is mainly due to the decrease of the nonradiative decay rate in polar solvents. The rate constant for radiative transition (k_r), which describes the electric dipolar coupling of the excited states with the ground states, and that for radiationless transition (k_{nr}), which describes the role of vibronic and spin–orbit interactions, can be determined using the following expressions:

$$k_r = \frac{\phi_f}{\tau_f} \tag{3}$$

$$k_{nr} = \frac{1-\phi_f}{\tau_f} \tag{4}$$

These decay parameters of DBBA at different solvent polarities were given in Table 2. The allowedness of the radiative emission reflected by a high ϕ_f and short τ_f and the absence of dual fluorescence do not point towards an excited state with a TICT character. The fluorescence of the dye is hence from ICT state [28].

4. Conclusions

Compound DBBA is sensitive to solvent polarity and it has high quantum yields, therefore it is a good material of photochemical probe. This functionality of this probe makes it potentially useful in laser dyes, fluorescence dyes, organic non-linear optic materials and biologically important systems. Future work directed to use DBBA as fluorescence probe for the determination of human serum albumin by fluorescence enhancing method is anticipated to be promising. Similar work is progress in our laboratory, and the results will be released soon.

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References

[1] Z.R. Grabowski, Pure Appl. Chem. 65 (1993) 1751–1756.
[2] M. Hashimoto, H. Hamaguchi, J. Phys. Chem. 99 (1995) 7875–7877.
[3] S.L. Wang, T.I. Ho, J. Photochem. Photobiol. A: Chem. 135 (2000) 119–126.
[4] A. Onkelinx, F.C. De Schryver, L. Viaene, M. Van der Auweraer, K. Iwai, M. Yamamoto, M. Ichikawa, H. Masuhara, M. Maus, W. Rettig, J. Am. Chem. Soc. 118 (1996) 2892–2902.
[5] A. Kapturkiewicz, J. Herbich, J. Karpiuk, J. Nowacki, J. Phys. Chem. A 101 (1997) 2332–2344.
[6] D. Braun, W. Retting, S. Delmond, J.F. Letard, R. Lapouyade, J. Phys. Chem. A 101 (1997) 6836–6841.
[7] K. Zachariasse, M. Grobys, E. Tauer, Chem. Phys. Lett. 274 (1997) 372–382.

[8] M.A. EI-Kemary, J. Photochem. Photobiol. A: Chem. 137 (2000) 9–14.
[9] W.J. Jin, W.H. Liu, X. Yang, Y.M. Zhang, G.L. Shen, R.Q. Yu, Microchem. J. 61 (1999) 115–124.
[10] Zh.L. Yan, Sh.K. Wu, J. Photochem. Photobiol. A: Chem. 96 (1996) 199–202.
[11] S.S. Atik, J.K. Thomas, J. Am. Chem. Soc. 104 (1982) 5868–5874.
[12] T. Nagamura, T. Kurihara, T. Matsuo, J. Phys. Chem. 86 (1982) 1886–1890.
[13] P.a. Brgger, P.P. Infelta, A.M. Braun, M. Gratzel, J. Am. Chem. Soc. 103 (1981) 320–326.
[14] M. El-Kemary, M. ElKhouly, M. Fujitsuka, O. Ito, J. Phys. Chem. A 104 (2000) 1196–1200.
[15] M. El-Kemary, M. Fujitsuka, O. Tto, J. Phys. Chem. A 103 (1999) 1329–1334.
[16] Y. Mo, F. Bai, D. Zhang, Z. Wang, D. Zhu, Sci. China (Series B) 39 (1996) 255–259.
[17] W. Verbouwe, L. Viaene, M. Van der Auweraer, F.C. De Schryver, H. Masuhara, R. Pansu, J. Faure, J. Phys. Chem. A 101 (1999) 157–165.
[18] W. Verbouwe, M. Van der Auweraer, F.C. De Schryver, J.J. Piet, J.M. Warman, J. Am. Chem. Soc. 120 (1998) 1319–1324.
[19] Z.B. Chen, Z. Zhang, T. Zhao, F.L. Bai, Y.P. Zhang, Z.T. Wang, Spectrochim. Acta (Part A) 57 (2001) 419–422.
[20] Z.H. Li, M.S. Wong, Y. Tao, M. D'Iorio, J. Org. Chem. 69 (2004) 921–927.
[21] D.B. Yao, T. Xie, Y.M. Gao, Wuli Huaxue Shouce, Shanghai, 1985.
[22] B.C. Reichardt, Angew. Chem. Int. Ed. Engl. 18 (1979) 98–110.
[23] J. Hicks, M. Vandersall, Z. Babaogic, K.B. Eisenthal, Chem. Phys. Lett. 116 (1985) 18–23.
[24] P.R. Bangal, S. Panja, S. Chakravorti, J. Phys. Chem. A 139 (2001) 5–16.
[25] S.A. Lyazidi, M. Dkaki, N. Bitit, D. Meziane, C.C. Dubroca, Ph. Cazeau, Spectrochim. Acta (Part A) 55 (1999) 89–94.
[26] Y.J. Wei, Z.M. Kang, X.J. Qi, Y.P. Zhang, C.G. Liu, Huaxue Xuebao 59 (10) (2001) 1619–1622.
[27] J.N. Demas, G.A. Crosby, J. Phys. Chem. 64 (1960) 762–764.
[28] B.B. Raju, B. Eliasson, J. Photochem. Photobiol. A: Chem. 116 (1998) 135–142.