Synthesis and Spectral Tuning of Novel Triphenylamine-Based Derivatives Containing Electron Donor-Acceptor Groups

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This paper presents the investigation of tuning the color and photoluminescence of a range of triphenylaminebased derivatives with various substituent groups. The ultraviolet/visible absorption and fluorescence spectroscopy of the derivatives showed remarkable difference. The molecular geometry optimization demonstrated that the properties of the ground state and the excited state of the compounds have a close relationship with the substituent groups. Therefore, it is possible to tune the color and photoluminescence of the derivatives at molecular level. The cyclic voltammograms of these compounds were detected in methylene chloride at various scan rates. The thermal stabilities of the compounds were analyzed with the different scanning calorimetry and the thermogravimetry.

Keywords spectroscopy, triphenylamine-core, stilbene derivatives, internal molecular charge transfer, molecular geometry optimization

Introduction

In recent years, the development of novel organic dyes with different color and photoluminescence has received considerable attention due to their applications in various areas such as material and biomedical fields.¹⁻¹⁴ In the search for high quality organic dyes with ideal spectroscopic nature, it was found that the spectral characteristics and applications of the dyes have a strong relationship with their chemical structures.^{15,16} Hence, the investigation of the effects of the chemical structures on the absorption and fluorescence spectroscopy of the compounds emerges as very important subjects in organic photochemistry and photophysics.¹⁷⁻²⁰

Bis(styryl)benzene derivatives with donor- π -donor, donor- π -acceptor and donor-acceptor-donor structural motifs have excellent optical properties,²¹ while two factors play key roles in the regulation of their molecular spectroscopic properties: (1) the conjugated length of the molecules, which could be tuned by the insertion of phenylene-vinylene or phenylene-butadienylene groups, (2) the extent of the symmetrical charge transfer from the ends of the molecules to the middle, or vice versa. These regulations could lead to a shift of the absorption and emission to longer wavelength compared to those of stilbene. In other words, the spectroscopic properties of these molecules could be affected by the extent of intramolecular charge transfer, which could be regulated by the substituent groups. Thus, the HOMO-LUMO gaps of the compounds can be tuned.

The electron-donating substituent groups, the conjugated length, and the medium have been successfully used to tune the optical properties of triphenylaminecored dves.^{22,23} However, the comparable investigations on the tuning spectroscopy of diphenylamine-cored dyes with electron-donating and electron-withdrawing groups were seldomly reported,²⁴ in particular, whether it is feasible to tune the color and photoluminescence of the dyes with electron donor-acceptor substituent groups has not been explored. In this paper, we employed various push-pull substituent groups, including nitro, formyl and methoxy groups, to tune the properties of the electron density distribution and the electron transition of the frontier orbitals of triphenylamine-cored stilbene derivatives with the aim to regulate their spectroscopic properties. As well known, nitro and formyl groups have electron-withdrawing nature, and methoxy group has electron-donating nature. Consequently, the extent of internal charge transfer of the derivatives could be different from each other. This means that the electron density distribution of chromophore part (i.e. stilbene part) of the dyes could be different from each other, which could cause different characteristics of the absorption and fluorescence spectroscopy. In order to deeply understand interrelationship between the chemical structures and the spectroscopic properties, the molecular geometry optimization and the electrochemical properties of the dyes were investigated in this article.

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Received November 1, 2009; revised January 6, 2010; accepted March 4, 2010.

Project supported by the National Natural Science Foundation of China (Nos. 20776165, 20702065, 20872184), Chongqing Science & Technology Commission (Nos. CSTC2008BA4020, CSTC2009BB4216), A Foundation for the Author of National Excellent Doctoral Dissertation of PR China (No. 200735) and Innovative Talent Training Project, the Third Stage of "211 Project" of Chongqing University (No. S-09103).



Figure 1 Chemical structures of the compounds studied in this paper.

Experimental

Reagents and materials

Organic solvents were obtained from Chongqing Medical and Chemical Corporation. Other chemicals and reagents were purchased from Aldrich unless otherwise specified. The organic solvents were dried using standard laboratory techniques according to well-known methods.²⁵ The starting materials were further purified with redistillation or recrystallization before use. Triphenylamine-cored stilbene derivatives (Figure 1) were synthesized in our laboratory.

Instruments

The UV/visible absorption spectra $(1 \times 10^{-5} \text{ mol/L})$ were recorded with a Cintra spectrophotometer. The fluorescence spectra $(1 \times 10^{-5} \text{ mol/L})$ were checked with Shimadzu RF-531PC spectrofluorophotonmeter. Rodamin 6G in ethanol ($\phi = 0.94$, $1 \times 10^{-6} - 1 \times 10^{-5}$ mol/L) was used as reference to determine the fluorescence quantum yields of the compounds herein.²⁶ To avoid self-quenching of fluorescence emission, low concentration of the samples $(1 \times 10^{-6} \text{ mol/L})$ was prepared for the survey of fluorescence quantum yields. The melting point was detected using a Beijing Fukai melting point apparatus. Nuclear magnetic resonance (NMR) spectroscopy was conducted at room temperature on a Bruker 500 MHz apparatus with tetramethylsilane (TMS) as an internal standard and CDCl₃ as solvent. Elemental analysis was performed by a CE440 elemental analysis meter from Exeter Analytical Inc.

The fluorescence quantum yields of the compounds in solvents with different polarities were measured based on the following equation:^{27,28}

$$\Phi_{\rm f} = \Phi_{\rm f}^0 \frac{n_0^2 A^0 \int I_{\rm f}(\lambda_{\rm f}) \mathrm{d}\lambda_{\rm f}}{n^2 A \int I_{\rm f}^0(\lambda_{\rm f}) \mathrm{d}\lambda_{\rm f}}$$

wherein n_0 and n are the refractive indices of the solvents, A^0 and A are the optical densities of the reference and the sample at excitation wavelength respectively, Φ_f and Φ_f^0 are the quantum yields of the reference and the sample respectively, and the integrals denote the area of the fluorescence bands for the reference and the sample respectively.

Molecular geometry optimization

The calculations were performed by means of the Gaussian 03 program package.²⁹ The geometry optimization on the ground electronic state (S₀) was carried out with HF method and at the DFT level using the B3LYP to calculate the energies;³⁰⁻³² while the CIS (Configuration Interaction Singles-excitation) has been employed to optimize the geometries of the first singlet excited state (S₁), and TDDFT (time-dependent DFT) was used to obtain the energies of **1** to **4**.

Electrochemistry

Electrochemical measurement was carried out using a Shanghai Chenhua working station. Two Pt work electrodes and an Ag/Ag⁺ reference electrode, namely

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three electrodes system, were included in cell. Typically, a 0.05 mol/L solution of tetra-*n*-butylammonium hexafluorophosphate in methylene chloride containing of dyes was bubbled with argon for 15 min before the measurement.

Thermal analysis

The differential thermal analysis (DTA) and thermograving (TGA) were conducted under nitrogen flow in Shimadzu DTG-60H equipment at the heating rate 10 $^{\circ}C \cdot \min^{-1}$.

Preparation of 1-4

The derivatives **1** to **4** are depicted in Scheme 1. 4-Formyl-triphenylamine and 4',4'-diformyl-triphenylamine were prepared according to well-known methods with modified procedure.³³

3,4,5-Trimethoxyl-benzylbromide 3,4,5-Trimethoxyl-benzaldehyde (30.6 mmol, 6.00 g) was deoxidized with sodium borohydride (40.7 mmol, 1.55 g) in 60 mL methyl alcohol. The reaction was performed at room temperature under argon for 2 h. After the reaction, the

Scheme 1 Synthesis route of derivatives 1 to 4

solvent was removed in vacuum after the filtration of the solid materials. The crude product was washed using water for five times. 3,4,5-Trimethoxyl-benzyl alcohol was purified with column chromatography using benzene as eluent. Yield 90%, color: light yellow, ¹H NMR (CDCl₃, 500 MHz) δ : 6.42 (s, 2H, ArH), 5.10 (s, 1H, ArCH₂OH), 4.52 (s, 2H, CH₂), 3.95 (s, 3H, ArOCH₃), 3.83 (s, 6H, ArOCH₃). Bromination of 3,4,5-trimethoxylbenzyl alcohol was carried out in tetrahydrofuran using phosphorus tribromide as bromine reagent under reflux. The solvent and excess phosphorus tribromide were removed in vacuum. The crude product was washed using distilled water for 5 times. 3,4,5-Trimethoxyl-benzyl bromide was purified with recrystallization in benzene/cyclohexane (V : V = 3 : 1). Yield 70%, color: white, m.p. 45–47 °C; ¹H NMR (CDCl₃, 500 MHz) δ : 6.35 (s, 2H, ArH), 4.10 (s, 2H, CH₂), 3.77 (s, 3H, ArOCH₃), 3.31 (s, 6H, ArOCH₃).

3,4,5-Trimethoxyl-4-benzylphosphonate (8) The compound was prepared by making 3,4,5-trimeth-oxyl-benzylbromide (11.53 mmol, 3.00 g) react with



triethyl phosphite (10 mL) at 130—160 $^{\circ}$ C for 6 h. After excess triethyl phosphite was removed in vacuum, the obtained crude 3,4,5-trimethoxyl-4-benzylphosphonate was directly used in the next step without further purification.

4-(3',4',5'-Trimethoxyphenylethylene)yl-triphenyl-3,4,5-Trimethoxyl-4-benzylphosphonate amine (1) (4.1 mmol, 1.32 g) was first mixed with 4-formyltriphenylamine (3.0 mmol, 0.82 g) in 50 mL dry tetrahydrofuran, then sodium methoxide (7.3 mmol, 0.39 g) was added as bases to initiate the reaction, which was proceeded at room temperature overnight. After the filtration of solid materials and vacuum evaporation of the solvent, the reactant mixture was dissolved in chloroform and washed by water. The organic layer was dried with anhydrous magnesium sulphate. After evaporated in vacuum, **1** was purified with column chromatography using benzene as eluent, which was further purified with recrystallization in methylene chloride. 1: Yellow solid, yield 55%, m.p. 62-63.5 °C; ¹H NMR (CDCl₃, 500 MHz) δ : 7.37 (d, J=8.5 Hz, 2H, ArH), 7.26 (t, J=8.0 Hz, 4H, ArH), 7.12 (s, 2H, ArCH=CH), 7.10 (s, 2H, ArH), 7.02–7.06 (m, 4H, ArH), 9.94 (d, J=7.5 Hz, 2H, ArH), 6.72 (s, 2H, ArH), 3.91 (s, 6H, ArOCH₃), 3.87 (s, 3H, ArOCH₃); ¹³C NMR (CDCl₃, 125 MHz) δ: 56.152, 60.994, 103.403, 123.083, 123.577, 124.532, 126.974, 127.290, 127.708, 129.316, 131.370, 133.433, 147.374, 147.559, 153.426. Anal. calcd for C₂₉H₂₇NO₃: C 79.61, H 6.22, N 3.20; found C 79.55, H 6.29, N 3.13.

4-(*p*-Nitro-phenylethylene)yl-triphenylamine (2) 4-Formyl-triphenylamine (1.00 mmol, 0.30 g) and p-nitro-phenylacetic acid (1.25 mmol, 0.23 g) were first thoroughly mixed, piperdine (0.3 mL) was then added. The mixture was heated at 100 $^{\circ}$ C for 2 h, than at 120 °C for 1 h until black solid was formed. The product was purified with column chromatography using benzene/ethyl acetate (V : V = 45 : 1) as eluent. Further purification was conducted with recrystallization in pure alcohol. 2: Red solid, yield 50%, m.p. 136–138 °C; ¹H NMR (CDCl₃, 500 MHz) δ : 8.20 (d, J=9.0 Hz, 2H, ArH), 7.60 (d, J=9.0 Hz, 2H, ArH), 7.41 (d, J=7.0 Hz, 2H, ArH), 7.18-7.22 (m, 4H, ArH), 7.11 (s, 1H, ArCH =CH), 7.07 (d, J=4.50 Hz, 4H, ArH), 7.06 (s, 1H, ArCH=CH), 7.04 (t, J=2.25 Hz, 4H, ArH); ¹³C NMR (CDCl₃, 125 MHz) *b*: 122.715, 123.600, 124.188, 124.986, 126.336, 128.001, 129.425, 132.896, 144.341, 146.399, 147.228, 148.580. Anal. calcd for C₂₉H₂₀N₂O₂: C 79.57, H 5.14, N 7.14; found C 79.65, H 5.20, N 7.06.

4-(3'',4'',5''-Trimethoxyl-phenylethylene)yl-4'-formyl-triphenylamine (3) 3,4,5-Trimethoxyl-4-benzylphosphonate (4.5 mmol, 1.43 g) reacted with 4,4'-diformyl-triphenylamine (1.5 mmol, 0.45 g) in 60 mL dry tetrahydronfuran using sodium methoxide (10.0 mmol, 0.85 g) as base at room temperature overnight. After the filtration of solid materials and the evaporation of solvents in vacuum, the reactant mixture was dissolved in chloroform and washed by water. The organic layer was dried with anhydrous magnesium sulphate. After evaporated in vacuum, 3 was purified with column chromatography using V(benzene) : V(AcOEt) = 45 : 1 as eluent, which was further purified with recrystallization in methylene chloride. 3: Yellow solid, yield 50%, m.p. 61—63 °C; ¹H NMR (CDCl₃, 500 MHz) δ : 9.83 (s, 1H, ArCHO), 7.70 (d, J=8.5 Hz, 2H, ArH), 7.46 (d, J =8.5 Hz, 2H, ArH), 7.36 (t, J=8.0 Hz, 2H, ArH), 7.17 -7.21 (m, 3H, ArH), 7.14 (d, J=8.0 Hz, 2H, ArCH= CH), 7.07 (d, J=8.5 Hz, 2H, ArH), 6.99 (s, 2H, ArH), 6.74 (s, 2H, ArH), 3.92 (s, 6H, ArOCH₃), 3.87 (s, 3H, ArOCH₃); ¹³C NMR (CDCl₃, 125 MHz) δ : 56.165, 60.990, 103.576, 119.922, 125.263, 125.981, 126.358, 127.193, 127.622, 128.419, 129.441, 129.805, 131.324, 133.022, 133.876, 138.044, 145.509, 146.029, 153.099, 153.451, 190.449. Anal. calcd for C₃₀H₂₇NO₄: C 77.40, H 5.85, N 3.01; found C 77.33, H 5.93, N 3.06.

4-(p-Nitro-phenylethylene)yl-4'-formyl-triphenyl**amine** (4) 4,4'-Diformyl-triphenylamine (1.70 mmol, 0.51 g) and *p*-nitro-phenylacetic acid (5.10 mmol, 0.91 g) were mixed fully and piperdine (0.5 mL) was added into the mixture. The resultant mixture was heated at 100 $\,^\circ C$ for 2 h, than at 120 °C for 1 h till black solid was formed. The product was purified with column chromatography using V(benzene) : V(ethyl acetate) = 45 : 1 as eluent. Further purification was conducted with recrystallization in anhydrous ethanol. 4: Red solid, yield 45%, m.p. 172—173 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 9.84 (s, 1H, ArCHO), 8.21 (d, J=9.0 Hz, 2H, ArH), 7.72 (d, J=9.0 Hz, 2H, ArH), 7.62 (d, J=9.0 Hz, 2H, ArH), 7.50 (d, J=8.5 Hz, 2H, ArH), 7.37 (t, J=6.8 Hz, 2H, ArH), 7.26 (d, J=3.0 Hz, 1H, ArCH=CH), 7.22 (d, J= 6.0 Hz, 1H, ArCH=CH), 7.17 (t, J=11.0 Hz, 5H, ArH), 7.10 (d, J=8.5 Hz, 2H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ: 120.522, 124.198, 125.496, 125.529, 125.738, 126.525, 126.770, 128.314, 129.866, 129.924, 131.334, 132.373, 132.410, 143.898, 145.925, 146.676, 146.781, 190.445. Anal. calcd for C₂₇H₂₀N₂O₃: C 77.13, H 4.79, N 6.66; found C 77.20, H 4.83, N 6.59.

Results and discussion

Synthesis

Among the different strategies to synthesize dyes, the most important factor is the choice of the base in the reaction. More byproducts were generated when sodium hydride was used to prepare 1 and 3 due to its strong alkalinity. While the alkalinity of sodium ethoxide was not strong enough to make the reaction occurred, sodium methoxide was demonstrated to be effective for the preparation of 1 and 3. Owing to the electronwithdrawing effect of nitro group of p-nitrophenylacetic acid and the electron-donating of triphenylamine core, 2 or 4 could be synthesized by heating condensation reaction of p-nitro-phenylacetic acid and 6 or 7 in very weak base such as piperidine. One of the key tricks for the preparation of **3** and **4** is the molar ratios of the starting materials. Although the cultivation of single crystals was failed, the pure products

were obtained by flash column chromatography and recrystallization. Clean ¹H NMR and ¹³C NMR spectra as well as narrow-range melting temperature of the dyes were obtained.

UV/visible absorption spectroscopy

A typical UV/visible absorption spectroscopy of 1 to 5 in benzene was presented in Figure 2. 1 and 2 exhibit double absorption peaks from 280 nm to 550 nm. The first absorption peak of 1 and 2 is similar to the absorption of triphenylamine-core, which indicates that this absorption band could be mainly from local electron transition of triphenylamine core. The second absorption peak of 1 and 2, namely the maximal absorption peak, could be ascribed to molecular (π, π^*) electron transition.³⁴ While as contrast, **3** and **4** display only one broad absorption band. The results imply that electron of formyl group could participate in the overall molecular electron hybridization to form π orbital, which causes a considerably broad absorption band. The results demonstrate that the electron transition of the derivatives could be altered by the substituent groups. The absorption spectral data of 1 to 4 in various solvents are listed in Table 1. The data show that the maximal absorption wavelength of the derivatives bearing with electron-withdrawing groups is much red-shifted, especially for 2 and 4 (2 to 1: ca. 60 nm red-shift). This is a strong indication that the long-wavelength absorption of triphenylamine-based stilbene derivatives could be assigned to highly allowed (π, π^*) electron transition with internal charge transfer.35 Owing to the role of electron-accepting substituent group, the extent of internal charge transfer of **3** could be larger than that of **1**. Likewise, the extent of internal charge transfer of 2 and 4 could be larger than that of 1 as well. This could lower the HOMO-LUMO energy gap of 2, 3 and 4, which could lead to the red-shift of the maximal absorption wavelength of 2, 3 and 4, and cause the different colors, as shown in Figure 3(a).

Fluorescence spectroscopy and fluorescence quantum yields

The maximal emission wavelength of the derivatives



Figure 2 UV/visible absorption spectra of 1 to 5 in benzene. *c*: 1×10^{-5} mol/L.

Table 1 Maximal absorption wavelength (λ_a) and the molar extinction coefficients (ε) of **1** to **4**^{*a*}

Compound				Solvent		
	Compound	Benzene	THF	EtOAc	CH_2Cl_2	CH ₃ CN
1	$10^{-5}\varepsilon$	0.234	0.284	0.231	0.248	0.327
1	λ_{a}	359.2	364.0	364.8	365.6	364.0
2	$10^{-5}\varepsilon$	0.322	0.261	0.310	0.300	0.310
	λ_{a}	420.2	422.8	428.0	429.2	419.2
•	$10^{-5}\varepsilon$	0.320	0.344	0.362	0.415	0.410
3	λ_{a}	364.0	368.8	370.4	376.0	372.0
4	$10^{-5}\varepsilon$	0.330	0.368	0.320	0.387	0.343
	λ_{a}	410.0	406.0	402.0	410.0	408.8

^{*a*} λ_a : nm, ε : mol⁻¹•L•cm⁻¹.



Figure 3 (a) Colors of **1** to **4** in benzene and (b) photoluminescence of **1** to **4** in benzene photoexcited by 365 nm.

with electron-withdrawing groups is red-shifted. Typical comparison of the fluorescence emission is presented in Figure 4. The fluorescence intensity of 2, 3 and 4 is much lower than that of 1, but their maximal emission wavelength is red-shifted with respect to that of 1. It is interesting that the fluorescence intensity of 4 is higher than 2, while its maximal absorption and fluorescence emission is blue-shifted with respect to that of 2, which indicates that the extent of internal charge transfer of 4 could be lower than that of 2.



Figure 4 Fluorescence spectra of **1** to **4** in benzene. $c: 5 \times 10^{-6}$ mol/L. Excited at 350 nm, slit widow: Ex: 1.5 nm, Em: 3 nm.

The maximal fluorescence emission wavelength and the fluorescence quantum yields of these compounds are presented in Table 2. As compared with 1, 2 exhibits 100-150 nm red-shift and 3 shows 50-60 nm bathochromic shift in various solvents. On the other hand, 1 has much larger relative fluorescence quantum yields than 2, 3 and 4. This could be ascribed to the greater extent of internal charge transfer of 2, 3 and 4, thus the electron density distribution in the stilbene part of the three derivatives is lowered, and the (π, π^*) electron transition is thus decreased, and the internal conversion (S_1, S_0) is increased.^{36,37} However, methoxy group increases the electron density distribution in stilbene part of 1, and its (π, π^*) electron transition is thus increased. Hence, 1 exhibits exceptionally excellent photoluminescence nature, as shown in Figure 3(b). Table 2 also suggests that the fluorescence emission of 2, 3 and 4 is much more sensitive to the polarity of the solvents. A typical comparison of the variation of fluorescence spectroscopy of 1 and 3 with the increasing of acetonitrile ratio in benzene/acetonitrile binary solvents is shown in Figure 5. The fluorescence spectroscopy of 3 shows remarkable change with the increasing ratio of acetonitrile. It is well known that intramolecular charge transfer is strongly dependent on the solvent po-

Table 2 Maximal fluorescence emission wavelength (λ_e : nm) and the fluorescence quantum yields (Φ) of 1 to 4

Compound		Solvent						
		Benzene	THF	EtOAc	CH_2Cl_2	CH ₃ CN		
	$\lambda_{ m e}$	418.0	431.0	430.0	442.0	451.0		
1	Φ	0.78	0.86	0.81	0.99	0.77		
	λ_{e}	540.0	582.0	589.0				
2	Φ	0.504	0.0623	0.0738	weak	weak		
	λ_{e}	471.0	480.0	486.0	498.0	510.0		
3	Φ	0.760	0.175	0.160	0.0251	0.00894		
	λ_{e}	526.0	564.0	558.0				
4	Φ	0.677	0.127	0.107	weak	weak		



Figure 5 Typical fluorescence spectra of 1 and 3 in various volume ratios of benzene/acetonitrile. (a) Excited at 350 nm, slit window: Ex: 1.5 nm, Em: 1.5 nm; (b) excited at 350 nm, slit window: Ex: 3 nm, Em: 3 nm.

larity.³⁸ Because **2**, **3** and **4** could have greater internal charge transfer properties, the fluorescence emission of these compounds is more sensitive to the solvent polarity.

Changes on the dipole moments between the excited state and the ground state

We further estimated the changes of the dipole moments between the excited state and the ground state based on Lippert equation:^{39,40}

$$hc(v_{\rm abs} - v_{\rm em}) = \frac{2\left(\mu_{\rm e} - \mu_{\rm g}\right)^2}{4\pi\varepsilon_0 a^3} \Delta f + \text{const}$$
(2)

$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) \tag{3}$$

wherein *h* is Planck's constant, *c* is the speed of light, and Δf is called the orientation polarizability. v_{abs} , v_{em} are the wavenumbers of the absorption and emission, *n* is the refractive index, and ε is the relative lowfrequency dielectric constant of the solvents.

Lippert equation considers the chromophore group as a dipole, which locates in a cavity with a radius of *a* in a continuous solvent-dipole environment, and this equation describes a solvent effect of the index of refraction

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and relative dielicetric constant. Consequently, the linear correlation between Stokes shifts and Δf do not reflect some special interaction between the fluorophore and solvent molecules such as hydrogen bonding. Because **2** and **4** exhibit too weak photoluminescence in polar solvents, we did not perform Lippert equation for these two derivatives. Figure 6 plotted the Stokes shift as a function of the solvent orientation polarizability (Δf) for the derivatives **1** and **3**. The linear correlations between Stokes shift and orientational polarizability indicates the dipolar solvent effects. The equations were obtained as follows:

1:
$$Y = 4392.5X + 3809.6$$
, 3: $Y = 3272.3X + 6089.7$

Thus, the dipole moment changes between the excited state and ground state could be calculated from the slopes. Table 3 shows that **3** does have larger dipole moment changes than **1**, which confirms that it has more internal charge transfer at the excited state.



Figure 6 Relationship between Stokes' shifts of **1**, **3** and the orientation polarizability (Δf) of solvents respectively.

 Table 3 Change of dipole moment between the excited state

 and ground state respectively obtained from experiments and

 theoretical calculations

Dipole moment change $\Delta \mu/D$	1	2	3	4
From experiment	2.419		2.433	
From theory ^{<i>a</i>}	0.581	3.068	-0.221	2.579
20				

 $1 \text{ D}=3.336 \times 10^{-30} \text{ C} \cdot \text{m}$, ^{*a*} in vacuum, for single molecule.

Geometry optimization

We utilized quantum chemical method to theoretically calculate the dipole moment changes between the excited state and ground state. Table 3 shows that the 2 and 4 have much larger dipole moment changes between the excited state and the ground state than 1, and the dipole moment change of 2 is larger than that of 4. The results suggest that the extent of internal charge transfer has an order of 1>2>4. We shall point out that the dipole moment changes between the excited state and ground state of 3 is smaller than that of 1 in theory, even it is a minus number. It is strange because the maximal absorption and emission wavelength of 3 is longer than that of 1, which means that dipole moment change of 3 should be larger than that of **1**. The main reason is that the theoretical calculation is based on the single molecule in vacuum, thus the solvent effect and solute-solute interaction is not considered. In vacuum, some negative charges are supposed to be transferred to carbon atom of formyl group and it results in the abnormally decreasing of dipole moment at the excited state in theory.⁴¹ The results in turn imply that the intramolecular charge transfer states of **3** could be destabilized by the solvents.

The HOMO and LUMO orbitals in the ground and excited states are further analyzed. Obvious internal charge transfer occurs in LUMO for the derivatives, as shown in Figure 7. We emphasize the comparison of 1/3and 2/4 respectively. Figure 7 shows that the electron density distribution is extensively distributed in formyl group of LUMO. As a consequence, the overlap extent of HOMO and LUMO of 3 is lower than that of 1, and the probability of (π, π^*) electron transition is decreased, and the fluorescence emission is diminished. Obviously, the electron density distribution of stilbene part 1 is higher and the (π, π^*) electron transition was thus strengthened,^{42,43} and the fluorescence is much enhanced. While for 2 and 4, formyl group offsets partly the electron-withdrawing effect of nitro group in the opposite position of LUMO, and the electron density distribution is distributed largely. Consequently, the overlapping extent of HOMO and LUMO of 4 is higher than that of 2, and the probability of (π, π^*) electron transition is enhanced, and thus 4 has a stronger emission than 2. Furthermore, Figure 7 demonstrates that the electron hybridization of π orbital of phenyl ring and n orbital (including the lone pair electrons of triphenylamine core and formyl group) takes place, and the emission is original from (π, π^*) electron transition.

Table 4 lists the theoretically calculated HOMO-LUMO gap in the S_0 and S_1 . As compared with that of 1, the smaller HOMO-LUMO energy gaps in the S₀ and S₁ of 2 and 4 could account for the red-shift of the maximal absorption and emission. It is interesting that the energy gaps of 4 are higher than those of 2 in the S_0 and S_1 , which interprets why the maximal absorption and emission of 4 is blue-shifted with respect to that of 2. While in theory, the HOMO-LUMO energy gaps of 3 are a little bigger than those of 1. The result was somewhat abnormal because that the absorption and emission spectroscopy of 3 are red-shifted with respect to 1. The reason could be the same as that which lead to abnormal dipole moment change of 3 in the excited state, which further indicates that the internal charge transfer state of 3 could be destabilized by the solvent effects and the HOMO-LUMO gaps are thus reduced in the solvents.

Cyclic voltammograms

The cyclic voltammograms of 1 to 4 were acquired at the scan rates from 50 to 200 mV \cdot s⁻¹. As shown in Figure 8, no corresponding redox potentials are observed which demonstrates that redox processes of the derivatives dyes are characterized with irreversible na-



Figure 7 Electron density distributions of frontier orbitals of 1 to 4 in the S_0 and S_1 .

Table 4	Energy gaps of HOMO a	and LUMO obtained from theor	etical calculations in the ground	state (S_0) and the excited state (S_1)
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	1		2		3		4	
	\mathbf{S}_0	\mathbf{S}_1	\mathbf{S}_0	\mathbf{S}_1	\mathbf{S}_0	S_1	S_0	S_1
$E_{\rm HOMO}/{\rm eV}$	-4.878	-5.656	-5.174	-5.034	-5.224	-5.863	-5.491	-6.409
$E_{\rm LUMO}/{\rm eV}$	-1.108	-1.505	-2.189	-2.375	-1.446	-1.784	-2.369	-2.565
Energy gap/eV	3.770	4.151	2.985	2.659	3.778	4.079	3.122	3.844

ture under all sweeping rates. The redox processes of 1 to 4 are dominated by the diffusion-controlled electron transfer reactions resulting from linear increasing of peak currents with the square root of scan rates.⁴⁴ The redox potentials of **1** to **4** at 0.1 V \cdot s⁻¹ scan rate are listed in Table 5. For comparison, the cyclic voltammograms of 5, 6 and 7 were detected. Seen from Table 5, the oxidation potentials of 1 to 4 (0.689, 1.102, 1.282, 1.111 V) could be assigned to triphenylamine-core. Firstly, we particularly compare the redox potentials of 1 and 2. Because nitro group is a powerful electron-withdrawing part and methoxy group is an electron-donating group, the first oxidation peak potentials of 2 (1.102 V) is higher than that of 1 (0.689 V). While, the first reduction peak of 1 (0.664 V) is higher than that of 2 (0.578 V). This implies that the electron-donating group lowers the oxidation peak potential of triphenylamine-core, while the electron-withdrawing group lowers the reductive potential of triphenylamine-core derivatives. Thus, the higher oxidation potential of 6 (1.229 V) and 7 (1.338 V) than 5 (1.028 V) could be ascribed to the electron-withdrawing role of formyl group as well. This is also explain why the first oxidation potential of 3(1.282 V) and 4 (1.111 V) is higher than that of 1 (0.689 V) respectively.

We further estimated HOMO-LUMO gap from the optical band gap (E_g) , which was calculated from the

onset of the longest absorption wavelength at ten percent of the maximal UV peak.^{47,48} Table 6 shows clearly that the HOMO energy of 2 is higher than that of 1, but its LUMO is smaller than that of 1. While, the energies of the HOMO and LUMO of 3 are lower than those of 1 respectively. Furthermore, the HOMO-LUMO gaps of 2 and 4 are lower than that of 1. The HOMO-LUMO gap of 3 is lower than that of 1, and the HOMO-LUMO gap of 4 is lower than that of 2 too. This suggests that not only the HOMO and LUMO energies of the derivatives could be mediated, but the HOMO-LUMO gaps could be regulated. These make it possible to tune the color and photoluminescence of the derivatives.

Thermal analysis

The analysis of the thermal properties was conducted with differential thermal analysis (DTA) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. The endothermic peaks determined by DTA were detected at 65.41, 144.11, 70.54 and 180.49 °C for **1** to **4** respectively as presented in Figure 9. If we consider that the heating rate was 10 °C•min⁻¹, the DTA data are fairly close to the melting points of these compounds determined with melting point apparatus. As shown in Figure 9, the exothermic peaks were detected at 397.41, 382.74, 403.90 and 331.89 °C for **1** to **4** respectively. Interestingly, **1** and **3** exhibit more thermal stability than



Figure 8 Cyclic voltammetries of 1 to 4 in methylene chloride at various scan rates.

Table 5 Redox potentials of 1 to 7 determined in methylene chloride at 0.1 V \cdot s⁻¹ scan rate

Derivative	Oxidation potential/V	Reduction potential/V		
1	0.689, 0.263	0.664, -0.718		
2	1.102	0.578, -0.194, -0.609		
3	1.282, 0.818	0.526, -0.354		
4	1.111, 0.916	0.762, 0.686		
5	1.028	0.42, -0.257, -0.567		
6	1.299	0.601, -0.468, -0.897		
7	1.388	0.707, -0.386, -0.749		

2 and **4**, which indicates that formyl group could be an important factor on the enhancement of thermal stability.

The weight loss of 1 (MW = 437.53) reached 81.244% at 397.41 °C, indicating the most of its chemical composition was decomposed and moved out

with nitrogen gas. The weight loss of 2 (MW = 392.45) was 52.65% at 382.74 °C, which is also close to the loss of nitro-styrene part (MW=225.24), meaning that the part of triphenylamine-core could be left. The weight loss of **3** (MW=465.54) was 51.29% at 403.90 °C, which is close to the loss of branches of 3 including (trimethoxystyrene)vl and formvl groups (MW: total= 252.30). Thus, the part of triphenylamine (MW = 245.32) could be left. The weight loss of 4 (MW=420.46) was 40.54%, which is close to the loss of the branches of 4including (nitrostyrene)yl and formyl groups (MW: total=207.22) as well. Likewise, the part of chemical composition of triphenylamine (MW=245.32) could be left. The analysis shows that the derivatives have good thermal stabilities, and the thermal stabilities of the derivatives have an interrelationship with their chemical structures.

 Table 6
 Estimated HOMO and LUMO energies of compounds 1 to 4 from cyclic voltammograms

Derivative	$\lambda_{\text{onset}}/\text{nm}$	Gap/eV	E^{OX}	$E_{\rm LUMO}/{\rm eV}$	$E_{\rm HOMO}/{\rm eV}$	$E_{\rm LUMO-HOMO}$
1	412.0	3.00	0.69	-5.03	-8.03	3.00
2	514.4	2.41	1.10	-5.44	-7.85	2.41
3	427.2	2.90	1.28	-5.62	-8.52	2.90
4	458.6	2.70	1.11	-5.45	-8.15	2.70

 $E_{\rm g} = 1240/\lambda$, LUMO (eV) = $-E^{\rm OX} - 4.34$,^{45,46} HOMO (eV) = LUMO $-E_{\rm g}$, $\lambda_{\rm onset}$: the longest absorption wavelength at ten percent of the maximal UV peak.



Figure 9 DTA and TGA of compounds 1 to 4.

Conclusions

New triphenylamine-core stilbene derivatives with various electron donor-acceptor groups were developed. The absorption and fluorescence spectroscopy of the derivatives could be efficiently tuned by the substituent groups. The substituent groups play significant roles on the electron transition properties of the derivatives. The electron density distribution in the frontier orbitals of the derivatives has a close relationship with the substituent groups, and thus the HOMO-LUMO gap could be mediated. These could be the deep reasons on the regulation of the spectroscopic properties of the derivatives. The measurements of DTA and TGA show that the thermal stability of the derivatives has a close relationship with their chemical structures.

Acknowledgements

We thank supports on the laser determination from the Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry (TIPC), Chinese Academy of Sciences.

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(E0911011 Cheng, B.; Zheng, G.)