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Synthesis and spectroscopic properties of conjugated triphenylamino-substituted chromophores

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Abstract

Two kinds of intramolecular conjugated charge-transfer triphenylamino-substituted chromophores 4-[2-(3-dicyanomethylene-5,5-dimethylcyclohex-1-enyl)-vinyl]triphenylamine (BHT) and 4,4′-bis[2-(3-dicyanomethylene-5,5-dimethyl-cyclohex-1-enyl)vinyl]triphenylamine (BDHT) were synthesized and characterized using ^{1}H NMR, FTIR and elemental analysis. Their spectroscopic properties were studied in solution and in MTES-, VTES-derived bulk materials. It was found that the chromophore with symmetrical structure (BDHT) enhanced fluorescence quantum yield more than that of the chromophore with asymmetrical structure (BHT). The solvatochromic behaviour of the chromophores in different solvents indicates that the peak wavelength of their solution fluorescence spectrum is related linearly to the solvent polarity ET (30) in the cases of certain solvents.

Keywords: Synthesis; Triphenylamine; Solvatochromism; Conjugated charge-transfer compounds; Fluorescence

1. Introduction

Conjugated organic materials exhibit a variety of interesting optical, electrical, photoelectric and magnetic properties in the solid state. The development of organic, electroactive and photoactive materials has progressed markedly in recent times due to their potential applications in molecular and supramolecular electronics, light harvesting and photocatalysis. In the meanwhile, they are also found to be important in optoelectronic devices, such as electroluminescence (EL) devices, photoconductors, light emitting devices (LED), solid-state lasers [1–3], biochemical fluorescent technology, non-linear optics, electrogenerated chemiluminescence and photovoltaic cells [4–10]. The advantage of organic over inorganic functional materials is the ease of processing and tuning of their properties through simple chemical modification. Among organic functional materials, intramolecular charge-transfer compounds are one of the most important molecular materials, which are functionalized by electron-donating (D) and electron-accepting (A) groups through a π-conjugated link. In the initially excited states, charge transfer and charge separation of these compounds endow them with unique optical and electric properties. The molecules with D–π–A structures have attracted much academic and technological research interest over the past few years because of their potential applications. By modifying the donors or/and acceptors, the properties of materials can be readily changed. As we know, there are two kinds of donor–acceptor structures, one is the asymmetrical structure D–π–A, such as 4-[2-(3-dicyanomethylene-5,5-dimethylcyclohex-1-enyl)vinyl]triphenylamine (BHT) and the other is the symmetrical structure D–π–A–π–D or A–π–D–π–A, as exemplified by 4,4′-bis[2-(3-dicyanomethylene-5,5-dimethyl-cyclohex-1-enyl)vinyl]triphenylamine (BDHT). As previous studies [11,12] reported that devices based on symmetrical molecules have better performance than those based on asymmetrical molecules, it is worthwhile to investigate the structure–functional property relationship of asymmetrical and symmetrical molecules.

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In this work, triphenylamine (TPA) was used as the electron-donating group [13,14] due to its excellent solubility, good stability, high photoluminescence (PL) efficiency and importance as a hole transport molecule in electrographic and electroluminescent devices, while 3-dicyanomethylidene-1,5,5-trimethylcyclohex-1-ene was employed as the electron-accepting group in the excited state, since it has excellent chemical, thermal and photochemical stability. We present the synthesis, characterization and spectroscopic properties of the two chromophores in both solution and bulk materials. Additionally, the solvatochromism in different solvents was examined to study the influence of solvent polarity on the absorption and emission wavelength of the two chromophores.

2. Experimental

2.1. Materials

Triphenylamine and isophorone were purchased from ACROS Organics and Lancaster Synthesis, Inc., respectively. 4-(Diphenylamino)benzaldehyde, phosphorus oxychloride ($POCl_3$) and malononitrile were obtained from Shanghai TL Chemical Co., Ltd., Shanghai Tingxin Chemical & Reagent Co. and Sinopharm Chemical reagent Co., Ltd., respectively. Reagent grade solvents were purified when necessary.

2.2. Instruments and measurements

Elemental analysis was carried out using an Eager 300 microelemental analyzer and ^1H NMR spectra were obtained with a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded on a Nicolet Avatar 360 in the region 4000–400 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) was carried out with a thermogravimeter (SDT Q600) under dry nitrogen gas flow at a heating rate of 10 °C min^{-1}. Glass transition temperatures (T_g) were measured using a DSC Q100 differential scanning calorimeter under a dry nitrogen gas flow at a heating rate of 10 °C min^{-1}. The solution- and bulk-phase UV–vis absorption and fluorescence emission of the two chromophores were recorded at room temperature; UV–vis absorption spectra were measured with a Hitachi Model U-4100 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

2.3. Synthesis of BDHT and BHT

2.3.1. 4,4′-Diformyltriphenylamine (**1**)

Compound (**1**) was prepared according to the literature [15]. Triphenylamine (4.900 g, 20 mmol) and anhydrous DMF (40 mL) were added to a 250-mL round bottomed flask under nitrogen. The mixture was cooled to 0 °C and phosphorus oxychloride (18.0 mL, 200 mmol) was added dropwise. The reaction mixture was heated at 85 °C for 10 h and the ensuing mixture was poured into ice water, neutralized to pH 7 with aq 2 N NaOH solution, extracted with dichloromethane and the solvent was removed. The crude product was collected by filtration and purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4/1) to obtain pure product. ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): δ 7.17–7.19 (m, 6H), δ 7.25–7.28 (t, 1H), δ 7.38–7.41 (t, 2H), δ 7.76–7.78 (d, 4H), δ 9.89 (s 2H, C*H*O). Anal. Calcd for $C_{20}H_{15}NO_2$ (301.34): C, 79.72; H, 5.02; N, 4.65; O, 10.62. Found: C, 79.65; H, 5.07; N, 4.75.

2.3.2. 3-Dicyanomethylidene-1,5,5-trimethylcyclohex-1-ene (ISO) (**2**)

A solution of isophorone (16.5 mL, 110 mmol), malononitrile (6.6 g, 100 mmol), piperidine (1.8 mL, 18.2 mmol), glacial acetic acid (0.40 mL, 7.0 mmol), and acetic anhydride (0.2 g, 2.0 mmol) in *N*,*N*-dimethylformamide (55 mL) was stirred at room temperature for 6 h and then refluxed at 120 °C for 4 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into water. The crude solid was collected and washed with brine, then treated with boiling water and filtered. Finally, the crude product was purified by using silica gel column chromatography (ethyl acetate/petroleum ether = 1/9). Brown crystals were obtained. Yield: 27%. ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): δ 1.04 (s, 6H, $CH_2(C\mathit{H}_3)_2CH_2$), δ 2.05 (s, 3H, $C\mathit{H}_3$), δ 2.20 (s, 2H, $C\mathit{H}_2(CH_3)_2CH_2$), δ 2.54 (s, 2H, $CH_2(CH_3)_2C\mathit{H}_2$), δ 6.64 (s, 1H, $C\mathit{H}{=}C$). Anal. Calcd for $C_{12}H_{14}N_2$ (186.25): C, 77.38; H, 7.58; N, 15.04. Found: C, 77.26; H, 7.80; N, 15.00.

2.3.3. 4-[2-(3-Dicyanomethylene-5,5-dimethylcyclohex-1-enyl)vinyl]triphenylamine (BHT) (**3**)

Aldehydetriphenylamine (0.273 g, 1.0 mmol) and 3-dicyanomethylidene-1,5,5-trimethylcyclohex-1-ene (0.186 g, 1.0 mmol) were dissolved in acetonitrile solution (20 mL). Piperidine was added as a catalyst and the mixture was refluxed for 10 h. The product precipitated from the solution and after washing with water, the pure product was obtained as fine dark red needles. Yield: 85%. FTIR (KBr pellet, cm^{-1}): 3032, 1591 (CH═CH), 2956, 2928, 2870 (CH_2), 2218 (CN), 1554 (Ar). ^1H NMR (500 MHz, $CDCl_3$, δ ppm): δ 1.07 (s, 6H, $CH_2(C\mathit{H}_3)_2CH_2$), δ 2.46 (s, 2H, $C\mathit{H}_2(CH_3)_2CH_2$), δ 2.59 (s, 2H, $CH_2(CH_3)_2C\mathit{H}_2$), δ 6.79 (s, 1H, $C\mathit{H}{=}C$), δ 6.84–6.87 (d, 1H, $C\mathit{H}{=}CH$, $J = 16$), δ 6.99–7.02 (m, 3H, Ar*H*), δ 7.09–7.14 (m, 6H, Ar*H*), δ 7.29–7.32 (d, 1H, $CH_2{=}C\mathit{H}_2$, $J = 16$), δ 7.30–7.36 (m, 5H, Ar*H*). Anal. Calcd for $C_{31}H_{27}N_3$ (447.48): C, 84.32; H, 6.61; N, 9.52. Found: C, 84.03; H, 6.23; N, 9.50.

2.3.4. 4,4′-Bis[2-(3-dicyanomethylene-5,5-dimethyl-cyclohex-1-enyl)vinyl]triphenylamine (BDHT) (**4**)

4,4′-Diformyltriphenylamine (0.301 g, 1.0 mmol) and 3-dicyanomethylidene-1,5,5-trimethylcyclohex-1-ene (0.558 g, 3.0 mmol) were dissolved in acetonitrile (20 mL). Piperidine was added as a catalyst and the mixture was refluxed for 10 h. The reaction mixture was cooled and poured into water and the product was extracted into CH_2Cl_2, and then dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the residue was purified by column chromatography (silica gel, CH_2Cl_2:petroleum ether, 3:1) to afford BDHT as a dark red solid with metallic luster. Yield: 58%. FTIR (KBr pellet, cm^{-1}): 3034, 1589 (CH=CH), 2954, 2926, 2870 (CH_2), 2216 (CN), 1556 (Ar). ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): δ 1.08 (s, 12H, $CH_2(CH_3)_2CH_2$), δ 2.46 (s, 4H, $CH_2(CH_3)_2CH_2$), δ 2.60 (s, 4H, $CH_2(CH_3)_2CH_2$), δ 6.81 (s, 2H, C*H*=C), δ 6.88−6.91 (d, 2H, C*H*=CH, $J = 16$), δ 7.00−7.03 (d, 2H, CH=C*H*, $J = 16$), δ 7.08−7.41 (m, 13H, Ar*H*). Anal. Calcd for $C_{44}H_{39}N_5$ (186.25): C, 82.86; H, 6.16; N, 10.98. Found: C, 82.55; H, 6.59; N, 10.29.

2.4. Preparation of bulk materials doped with chromophores

Methyltriethoxysilane (MTES)- and vinyltriethoxysilane (VTES)-derived bulks were prepared as follows. The initial sol was prepared by a multistep sol−gel route involving the acid-catalyzed hydrolysis and base-catalyzed condensation of VTES or MTES precursor at room temperature; the molar ratio of VTES or MTES:ethanol:water was 1:3:3. After hydrolysis with HCl as acid catalyst (pH = 2.5) for 1 h, a small amount of amine-modified silane *N*-(3-(triethoxysily)-propyl)-ethylenediamine was added as basic catalyst (pH = 5−6), followed by additional stirring for 30 min. THF solvent containing the chromophore (BHT or BDHT) was added dropwise to the sol followed by 30 min stirring. The initial molar concentration of BHT or BDHT in the MTES- and VTES-derived sol was $1 \times 10^{-4}\ \mathrm{mol\,L^{-1}}$. The obtained sol was sealed in a Teflon beaker and dried and aged in an oven at 40 °C. The MTES- and VTES-derived bulks were single-face polished before the fluorescence experiment.

3. Results and discussion

3.1. Synthesis and characterization of BHT and BDHT

Scheme 1 shows the pathway for the synthesis of BHT and BDHT. For photoelectronic application, organic materials with high glass transition and decomposition temperatures are critical for device stability and good lifetime. Thermogravimetric analysis (TGA) indicated that BHT exhibited an onset of decomposition at a temperature > 290 °C with no mass loss at lower temperature (Fig. 1); partial decomposition of BDHT was found to occur at about 120 °C.

The glass transition temperatures (T_g) of the two molecules were determined using differential scanning calorimetry (DSC). Since the chromophores used in OLED devices are always amorphous, the two molecules were heated and cooled quickly and then heated again to examine the amorphous glass transition temperature. All of the DSC curves are depicted in Fig. 2. BHT exhibited two crystalline melting peaks at 125 and 164 °C in the first heating trace of the DSC curve, attributed to different crystal structures in BHT since they were precipitated directly from the solution. If cooled quickly from the melting point, it has a $T_g = 66$ °C, whereas the glass transition of BDHT is at 111 °C. The T_g of BDHT is much higher than the commonly used hole transporting materials NPB (96 °C) [16].

3.2. UV−vis absorption and fluorescence emission spectra in solution

The spectroscopic properties of absorption and fluorescence emission spectra are listed in Table 1. Fig. 3 shows the absorption spectra of BHT and BDHT in toluene. Both exhibited broad absorption bands from 400 to 550 nm, the maximum absorption wavelength of the two chromophores were 489 and 504 nm, respectively, corresponding to the charge-transfer transition from the electron-rich TPA core to the electron-deficient ISO moiety. The λ_{max} of BDHT was bathochromically shifted by about 15 nm, when compared to BHT. The symmetrical structure of BDHT permits increased charge-transfer character in the excited state [17]. A larger π-delocalization system might be expected in BDHT, resulting in the observed red shift of the absorption maximum.

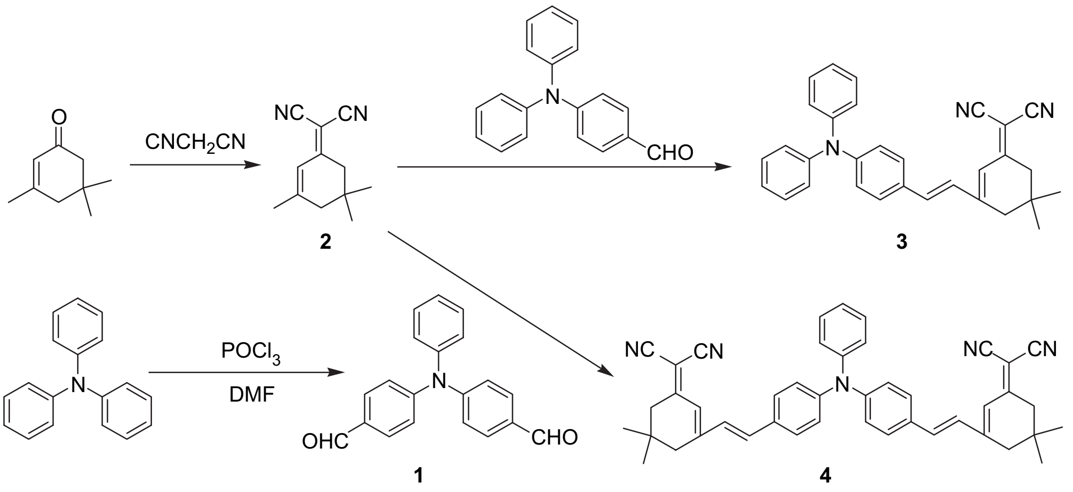
The UV−vis absorption spectra of BHT conducted in ethyl acetate, acetonitrile and methanol solutions show marked positive solvatochromism. From ethyl acetate to methanol, with an increase in the solvent's polarity, the peak located at the long wavelength can be attributed to the charge-transfer complex red shifted gradually due to stabilization of the charge-transfer complex in polar solvents [18]. The fluorescence emission spectra (Fig. 4) show shifts similar to those observed in the absorption spectra, and the emission intensity in ethyl acetate at 637 nm was much stronger than in the other two solvents; the peak intensity decreased by a factor of 1/16 in acetonitrile and 1/25 in methanol, compared with ethyl acetate.

More significant differences were observed when comparing fluorescence spectra which show photoluminescence in the red region. The emission band of BHT was much broader than that of BDHT. The emission maximum band shifts to longer wavelength in the order BHT < BDHT, by about 20 nm. Moreover, the fluorescence intensity significantly increased in the same order, the intensity of BDHT being about six times greater than that of BHT. The quantum yields of BHT and BDHT were 0.0275 and 0.0949, respectively, by comparing the absorption and emission spectra results to those of a quantum yield known standard (PM 567, $\eta = 0.5$ in toluene) according to Eq (1) [19]:

$$\frac{\eta_1}{\eta_2} = \frac{S_1 h_2}{S_2 h_1}, \tag{1}$$

where h_i is the absorption peak height, S_i the area enclosed by the emission curve and the wavelength axis of the emission spectrum and η_i is the quantum yield. The subscripts 1 and 2 refer to two measured dyes, respectively.

The photoluminescence characteristics were found to depend on the dimensionality of the molecules. The two-branched compound (BDHT) exhibited a higher fluorescence quantum yield than its one-branched analogue, which might be ascribed to slower nonradiative decay [20]. The absorption maxima, as well as the fluorescence peak wavelengths, of the



Scheme 1. Pathways for the synthesis of BDHT and BHT.

two molecules were abnormal in toluene with respect to other solvents (Table 1), in view of the lower ET (30) value of toluene. A proper explanation could be the additional interaction between the solvent and aromatic solvents such as toluene [19].

3.3. Fluorescence emission spectra in bulk materials

For further understanding of the spectroscopic properties of the chromophores, the fluorescence emission in bulk materials was studied (Fig. 5). When compared with the fluorescence spectra performed in solvents, there are obvious differences.

First of all, the fluorescence intensities of BHT and BDHT are quite different. In solvents such as toluene, the intensity of BDHT is six times stronger than that of BHT. However, in bulk materials, although the fluorescence intensity of BHT is still stronger, it is not so distinct. Indeed, the extent of the difference could even be ignored since the distinction in solvents is well distinguished. This finding can be ascribed to the solvatochromism of the two chromophores. As the charge density of BHT is much larger than BDHT, it leads to much smaller fluorescence intensity of BHT in polar solvents. As solvation ability will decrease greatly in a rigid solid medium with respect to a solution, the intensities and the emission peaks will be almost the same.

Second, the bulk materials with a different precursor (MTES or VTES) display good differentiation, BHT < BDHT and MTES < VTES, in terms of fluorescence emission intensity. For example, no matter whether BHT or BDHT, the emission intensity in the VTES-derived bulk was stronger than in the MTES-derived bulk. This can be attributed to the remaining ''polarity'' caused by the functional group of the precursor. The ''polarity'' of the solvent or bulk will influence fluorescence intensity insofar as the greater the ''polarity'' of the solvent or bulk, the lower the fluorescence of the chromophore will be. This phenomenon could be attributed to stabilization of the charge-transfer structure of the molecule. Since the ''polarity'' of MTES is larger than that of VTES, this results in the

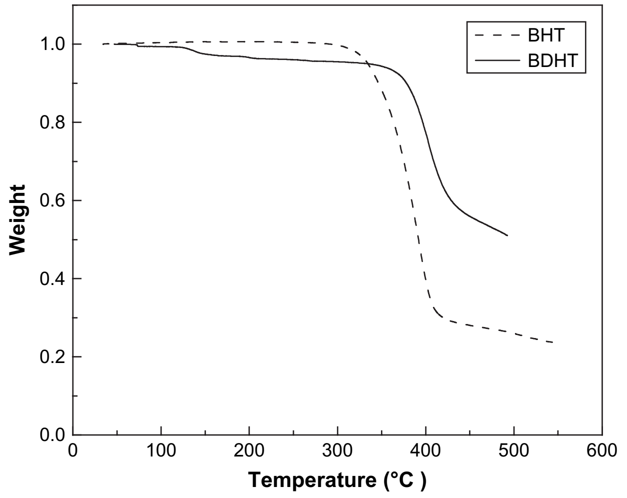


Fig. 1. TGA curves of BHT and BDHT.

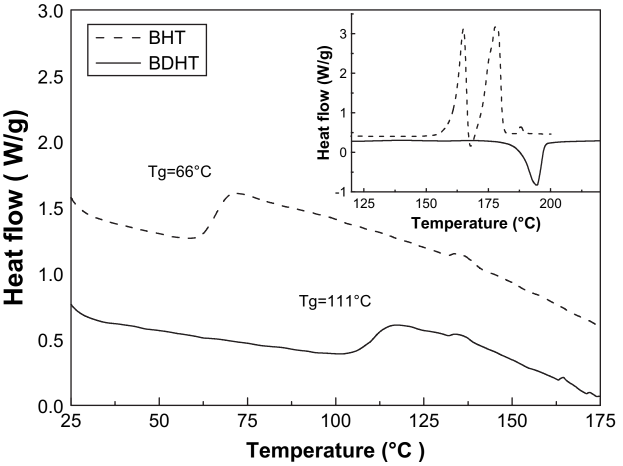


Fig. 2. DSC curves of BHT and BDHT in the second heating process after quickly cooled from the melting point. Inset shows the DSC curves in the first heating process.

Table 1
Spectroscopy properties and Stokes shift of BHT and BDHT

Solvent	ET (30) [22] (kJ mol^{-1})	λ (nm)				Stokes shift of BHT (nm)	Stokes shift of BDHT (nm)
		Absorption of BHT	Fluorescence of BHT	Absorption of BDHT	Fluorescence of BDHT		
Toluene	142	489	590	504	589	101	85
Ethylether	145	477	610	499	613	133	114
Ethyl acetate	160	477	633	504	638	153	134
Dichloromethane	172	492	660	520	665	168	145
Acetone	177	482	677	509	670	195	161
Acetonitrile	193	478	702	505	716	224	211
Ethanol	217	491	670	516	653	179	137
Methanol	233	484	677	510	677	193	167

fluorescence in MTES-derived bulk being much lower than that in VTES.

Similarities were also observed between the bulk materials and solvents in that BDHT displayed better fluorescence emission than BHT both in the bulk and solvent media. When we compared the structures of the emission band of BDHT and BHT, for instance in the VTES-derived bulk materials, it is clear that the former had a broader band which was the same in case of the solvents.

3.4. Analysis of solvatochromism

As mentioned above, the two chromophores show remarkable solvatochromism in different solvents and the D–π–A conjugated materials will have highly polar, excited electronic structures as a result of electron transfer from the donor to the acceptor. It is therefore worthwhile to study the solvatochromism of the chromophores in different solvents in order to know more about the relationship between polarity and molecular structure [21]. The solvatochromism of chromophores is usually determined from their Stokes shifts. Table 1 shows that the Stokes shift of BHT was larger than that of BDHT, especially in polar solvents. Similar results were obtained by calculating the difference between the frequencies of their absorption (ν_a^{max}) and emission maxima (ν_F^{max}) in various solvents, of the form [22]:

$$\Delta\nu_s = \nu_a^{max} - \nu_F^{max} = A + \mathrm{BK}\left[2\left(\mu_e - \mu_g\right)^2/hca^3\right], \tag{2}$$

where h is the Planck constant, c the speed of light, a the radius of the Onsager cavity, μ_g the dipole moment for the chromophore in its ground electronic state, and μ_e that in the excited electronic state involved in the transition considered and BK in relation (2) can be defined by [23]:

$$\mathrm{BK} = \left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right) \Big/ \left[\left(1-\frac{n^2-1}{2n^2+1}\right)^2\left(1-\frac{\varepsilon-1}{2\varepsilon+1}\right)\right], \tag{3}$$

where n is the refractive index of the solvent and ε is the dielectric constant.

Fig. 6 shows the values of $\Delta\nu_s$ for BHT and BDHT in different solvents against their values of BK from which it is evident that a linear relationship exists except for the two solvents. When the value of $\mu_e - \mu_s$ was calculated from the slope of the figure, values for BHT and BDHT were 1.22×10^{-28} C m and 1.78×10^{-28} C m, respectively.

Fig. 7 shows that a linear relationship was obtained between the empirical parameter of solvent polarity, ET (30) and the peak wavelength of fluorescence spectrum in solution

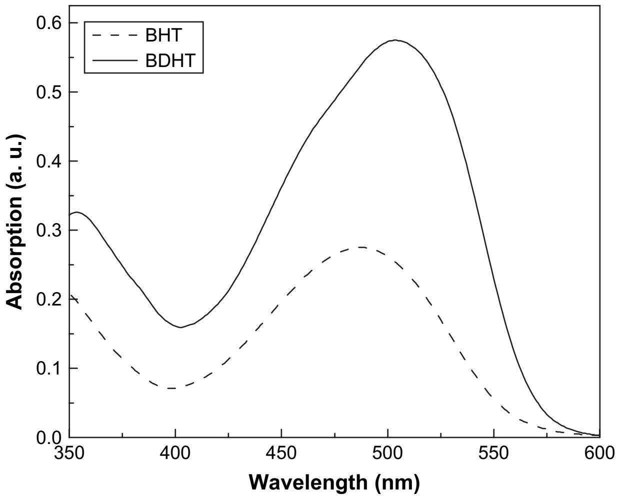


Fig. 3. UV–vis absorption spectra of BHT and BDHT in toluene.

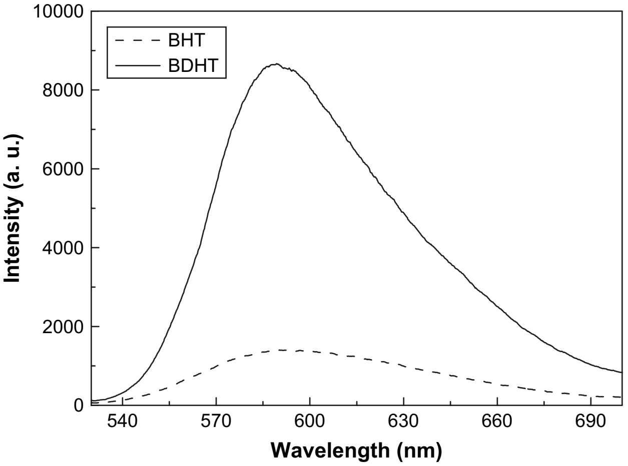


Fig. 4. Fluorescence spectra of BHT and BDHT in toluene.

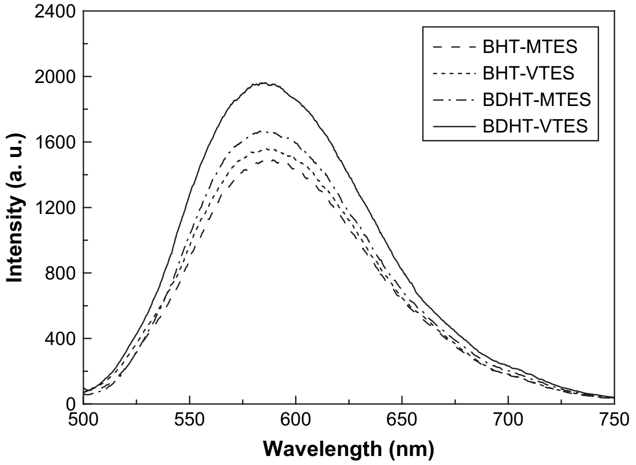


Fig. 5. Fluorescence spectra of BHT and BDHT in MTES- and VTES-derived bulk materials.

[22] except for ethanol and methanol. This may be due to the increasing polarity of the solvent under which, the excited electron transfer structure of the chromophores would be more stable; a more stable structure will shift the $\lambda_{\max}$ and emission spectra to longer wavelength. In the case of ethanol and methanol, for which a non-linear relationship was found, the cause may be poor dissolution of the two chromophores in the solvents.

4. Conclusions

Two conjugated triphenylamino-substituted chromophores, BHT and BDHT, with one and two electron-acceptor groups (ISO) were synthesized and characterized by elemental analysis, ^{1}H NMR, FTIR, UV–vis spectra and thermogravimetric analysis (TGA). The introduction of additional electron-acceptor groups into the chromophore resulted in a symmetrical structure, which enhanced fluorescence quantum yield in both bulk and solvent media, when compared with the asymmetric chromophore. The solvatochromism of BHT and BDHT exhibited a linear relationship as obtained from the plots of $\Delta\nu_s$ as a function of BK.

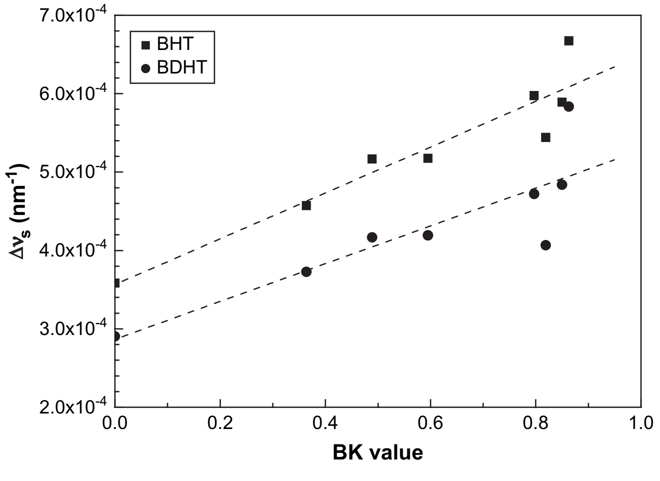


Fig. 6. Value of $\Delta\nu_s$ for BDHT and BHT in different solvents against their value of BK.

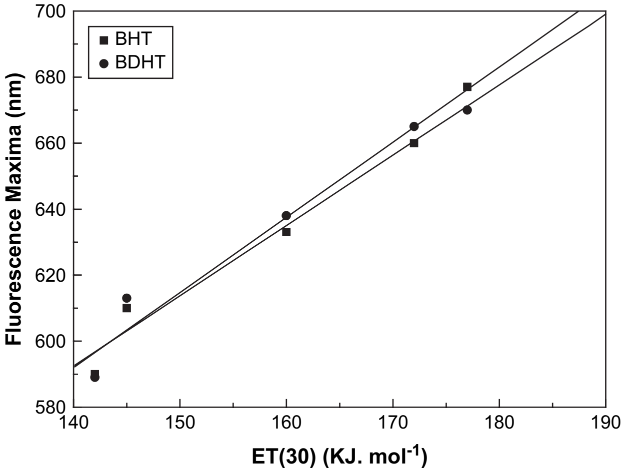


Fig. 7. Fluorescence maxima of BHT and BDHT against the empirical parameter of solvent polarity ET (30).

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