

Synthesis, photophysical and electrochemical properties of 2,8-diaryl-dibenzothiophene derivatives for organic electronics

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Abstract. A series of 2,8-*p*-diaryldibenzothiophene derivatives were synthesized and characterized. These molecules have electron withdrawing or electron donating groups at the *para* phenyl position, which alters the electronic properties of these derivatives. The quantum yield, fluorescence lifetime, singlet, triplet and E_{HOMO} energy levels of these compounds were determined by fluorescence, phosphorescence and cyclic voltammetry. A plot of Hammett constants of the *para* substituents vs E_{HOMO} revealed a linear relationship. The usefulness of these molecules in organic light emitting diodes, OLEDs is discussed vis-à-vis the energy levels and properties.

Keywords. Dibenzothiophene; Suzuki–Miyaura coupling; palladium catalyst; phosphorescence; triplet OLED; hole blocker.

1. Introduction

The interest in new organic materials for electronic applications has grown tremendously over the last decade due to enormous market opportunities. The synthetic versatility and favourable optical and electronic properties offered by thiophene containing compounds make them materials of choice for non-linear optical, organic light-emitting, light-harvesting, and transistor devices.^{1–3} In addition to desirable macroscopic device characteristics, such as luminescence efficiencies and low drive voltages for OLEDs and organic field-effect transistor (OFETs), an insight into the optical and electronic properties is also required to elucidate structure–function relationships. The photophysical study of pyrrole derivatives,⁴ oligo- and polythiophenes⁵ and other heterocycles⁶ have been explored in detail. However, reports on the optical properties of embedded thiophenes, particularly dibenzothiophenes, are scarce.^{7–9}

An understanding of the photophysical properties of organic materials is fundamental to the understanding of the functioning in many applications.^{5,10,11} The triplet energy levels of many conjugated materials have not been estimated due to difficulties in measuring their low-intensity phosphorescence.⁵ As a

result, the triplet energies of widely used systems such as oligothiophenes and oligomers of the *para*-phenylene have been reported only recently.^{5,12–14} The knowledge of triplet energy levels is important in choosing the correct conjugated organic host/guest materials in energy transfer processes. For example, long lived electro-phosphorescence from organometallic phosphor is efficient when the triplet excited state of the host material is higher than that of the dopant to prevent quenching of the dopant emission by back transfer.¹⁵ In OLEDs, optimum alignment of triplet energy levels is required for triplet energy transfer and hence to improve the performance of doped^{16–18} devices. In donor–bridge–acceptor (DBA) systems, also, the alignment of the triplet energy levels improve the electroluminescence efficiency.¹⁹ Therefore, it is essential to determine the triplet energies of conjugated organic materials in addition to determination of HOMO, LUMO, S_1 energy levels and quantum yield for optoelectronic devices.²⁰

In this paper, we describe the synthesis of diaryldibenzothiophene derivatives 1–4 and study their physical properties. Specifically, we describe the singlet and triplet state properties of 1–4 by absorption, fluorescence, phosphorescence, time resolved emission in the nanosecond time regime and electrochemical studies. We discuss the effect of

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electron withdrawing and electron donating groups on energy levels, emission and electrochemical properties of dibenzothiophene derivatives.

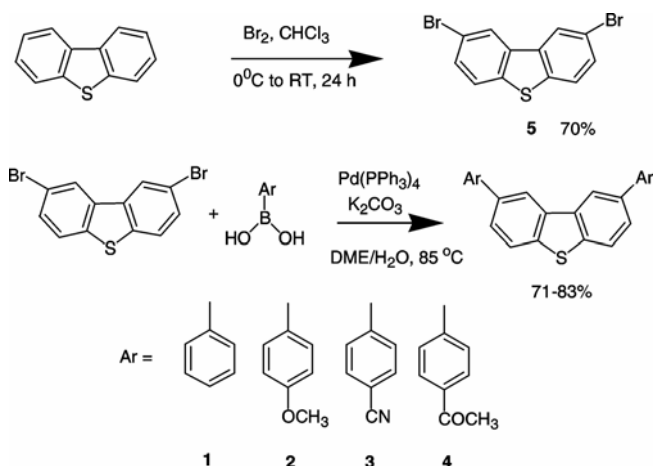
2. Experimental

All the solvents were obtained from SD Fine Chemicals (India). Aryl boronic acid(s), dibenzothiophene, K_2CO_3 , were purchased from Sigma-Aldrich and were used as received. $Pd(PPh_3)_4$ was freshly prepared using $PdCl_2$ and PPh_3 . Reactions were carried out under inert atmosphere of nitrogen in oven-dried glasswares. Progress of reaction was monitored using Silica Gel TLC plates and UV detection (254 and 365 nm). Silica gel (100-200 mesh) was used for column chromatography.

1H and ^{13}C NMR spectra were recorded using Bruker spectrometer with working frequency of 500 MHz for 1H NMR and 125 MHz ^{13}C NMR. The chemical shifts were referenced to TMS (added) or $CHCl_3$ present as impurity in $CDCl_3$. Mass spectra were measured using MALDI-TOF mass spectrometer. Photoluminescence were measured using SPEX Fluorolog 1681. Quantum yield were calculated using Anthracene standard. Photoluminescence decays were measured using Time Correlated Single Photon Counting (TCSPC) method. Cyclic voltammetry was done using CH Instruments 600°C. Oxidation potentials were determined with respect to ferrocene as internal standard.

2.1 Synthesis of 1–4

Diaryldibenzothiophene derivatives, 1–4 were synthesized as shown in scheme 1. 2,8-dibromo-



Scheme 1. Synthetic scheme for dibenzothiophene derivatives 1–5.

dibenzothiophene, **5** was obtained by selected bromination at 2- and 8-positions of dibenzothiophene²¹ using bromine solution in chloroform at 0°C. Recrystallization of crude product with methanol gave **5** as white solid in 70% yield. Dibenzothiophene derivatives **1–4** were prepared by Suzuki–Miyaura coupling.²² 2,8-Dibromo-dibenzothiophene (0.58 mmol), arylboronic acid (1.26 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.026 mmol) and K_2CO_3 (0.42 g, 2.9 mmol) were placed under inert atmosphere in a reaction vessel. 1,2-Dimethoxyethane (6.0 mL) and water (6.0 mL) were added while purging argon. The reaction mixture was stirred at 85°C for approximately ~24 h. After cooling the reaction mixture to room temperature, dichloromethane was added and organic layer was separated from aqueous layer. Aqueous layer was washed three times with dichloromethane. All organic layers were combined and washed with brine and dried over Na_2SO_4 . The solvent was evaporated to get the crude product. Silica gel column chromatography using a mixture of hexanes and ethyl acetate (9 : 1) as eluent afforded the pure compound in good yields, **1** (75%), **2** (78%), **3** (83%) and **4** (71%) as white solids. Compounds **1–4** were characterized by 1H NMR, ^{13}C NMR, MALDI-TOF, FT IR etc. All the compounds **1–4** were stable in air.

2.1a Characterization data for 2,8-diphenyl-dibenzothiophene, 1: M.P. 147°C; 1H NMR (500 MHz, $CDCl_3$): 8.42 (s, 2H), 7.93 (d, 2H, $J = 8.3$ Hz), 7.73 (d, 6H, $J = 7.2$ Hz), 7.50 (t, 4H, $J = 7.6$ Hz), 7.39 (t, 2H, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 141.11, 139.00, 138.01, 136.10, 128.98, 128.77, 127.90, 127.29, 126.37, 125.75, 123.44, 122.77, 120.39, 120.17, 119.74; MALDI-TOF (m/z) for $C_{24}H_{16}S$ Calcd. 336.45, Obsd. 336.89.

2.1b Characterization data for 2,8-di-(4-methoxyphenyl)-dibenzothiophene, 2: M.P.: 184°C; FT IR: 2836 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): 8.35 (s, 2H), 7.90 (d, 2H, $J = 8.3$ Hz), 7.65–7.68 (m, 6H), 7.05 (d, 4H, $J = 8.6$ Hz), 3.38 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 159.21, 138.38, 137.60, 136.16, 133.70, 128.89, 128.38, 128.34, 125.99, 123.34, 122.92, 120.07, 119.65, 119.05, 114.39, 53.36; MALDI-TOF (m/z) for $C_{26}H_{20}O_2S$ Calcd. 396.50, Obsd. 396.75.

2.1c Characterization data for 2,8-di-(4-cyanophenyl)-dibenzothiophene, 3: M.P. 286°C FT-IR: 2223 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): 8.41 (s, 2H), 8.00 (d, 2H, $J = 8.3$ Hz), 7.78–7.83 (d-d, 8H,

$J = 11.0$ Hz and $J = 8.3$ Hz), 7.73 (*d*, 2H, $J = 8.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3): 145.42, 140.48, 136.11, 132.84, 127.80, 128.22, 125.78, 123.92, 120.23, 118.82, 111.09; MALDI-TOF (m/z) for $\text{C}_{26}\text{H}_{14}\text{N}_2\text{S}$ Calcd. 386.47, Obsd. 386.86

2.1d Characterization data for 2,8-di-(4-acetylphenyl)-dibenzothiophene, **4**: M.P. 212°C FT IR: 1680 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): 8.45 (*s*, 2H), 8.10 (*d*, 4H, $J = 8.4$ Hz), 7.97 (*d*, 2H, $J = 8.3$ Hz), 7.83 (*d*, 4H, $J = 8.4$ Hz), 7.76 (*m*, 2H), 2.67 (*s*, 6H); MALDI-TOF (m/z) for $\text{C}_{28}\text{H}_{20}\text{O}_2\text{S}$ Calcd. 420.52, Obsd. 421.02.

3. Results and discussion

Absorption spectra of **1–4** were recorded in dichloromethane (figure 1) and the spectral data are summarized in table 1. The UV-Vis spectra of **1–4** showed two major absorption bands and a weak ($\log \epsilon < 4$) long wavelength band for **1** and **2**. The substitution of methoxy, cyano or acetyl at the *p*-phenyl position causes a bathochromic shift of the intense absorption band at 286 nm for **1** to 303 nm for **4**.

Steady state fluorescence spectra of **1–4** were recorded in dichloromethane, which are shown in figure 2. The fluorescence peak showed a large Stokes shift (70–110 nm) with respect to the absorption peak (286–303 nm) for all the molecules. The peaks in excitation spectra were matching with those in absorption spectra. The large red shift is attributable to excited state relaxation presumably involving

charge transfer excited state with a large dipole moment.

The molecules were fluorescent in the solid state indicating absence of self quenching. Figure 3 shows fluorescence spectra of the molecules in thin film. The fluorescence peaks in solid state showed little red shift with respect to the solution spectra for molecules **1**, **2** and **4**. For **3**, the cyanophenyl derivative, the fluorescence spectrum in the solid was red shifted by 42 nm. Red shift of spectra in solid state is common for most luminescent organic molecules. While a slight red shift can be attributed to the fact that optical transition energy depends on the dielec-

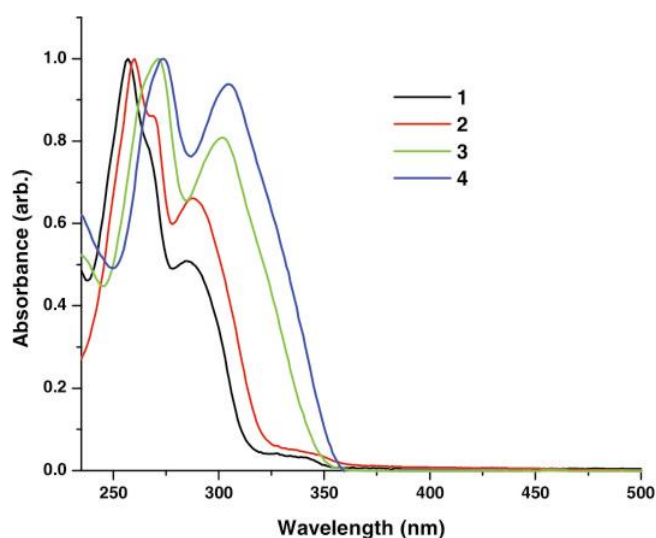


Figure 1. Normalized absorption spectra of **1–4** in dichloromethane.

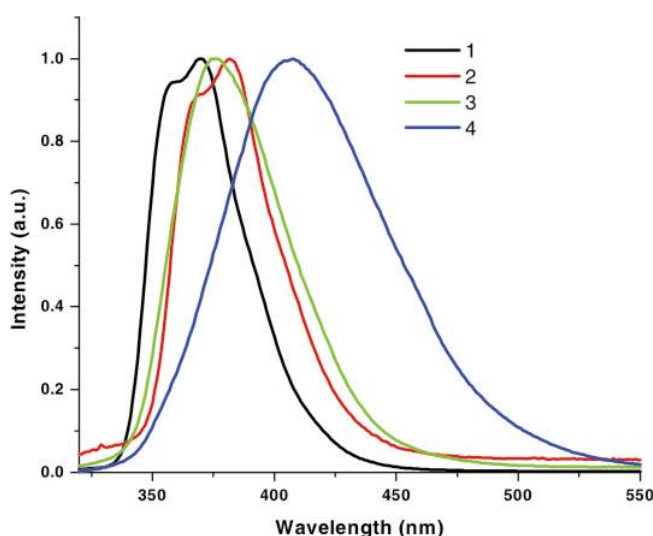


Figure 2. Normalized fluorescence spectra of **1–4** in dichloromethane.

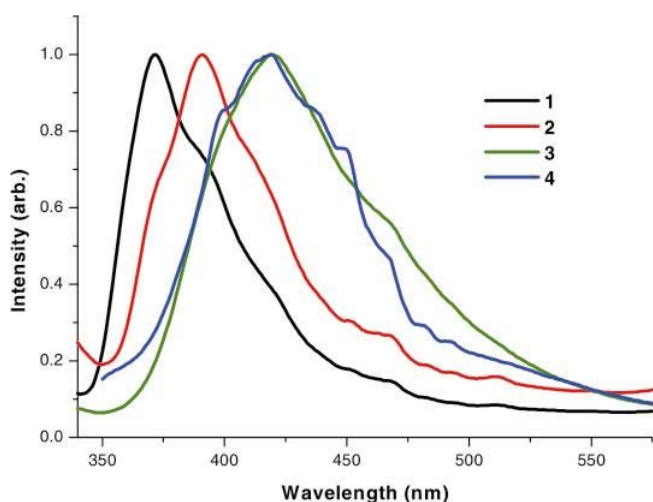


Figure 3. Normalized thin film fluorescence spectra of **1–4**.

Table 1. Photophysical data of 1–4.

Compound	Absorbance ^a nm (log ϵ)	λ_{fl} (nm) ^a	λ_{fl} (nm) ^b	λ_{ph} (nm) ^b	τ (ns) ^a	τ (ns) ^b	ϕ (%) ^a	ϕ (%) ^b	$S_0 - S_1$ (eV)	$S_0 - T_1$ (eV)
1	256 (4.52), 286 (4.25), 333sh (3.52)	356, 374	371	502	0.90	0.82	3	2.7	3.49	2.70
2	259 (4.81), 288 (4.63), 340sh (3.59)	367, 384	390	500	1.06	1.13	4	4	3.40	2.63
3	271 (4.85), 301 (4.75)	377	419	508, 544	0.90	0.70	15	11.7	3.23	2.51
4	275 (4.51), 303 (4.54)	415	419	511, 541	0.27	0.08	2	0.3	3.25	2.51

^aIn dichloromethane, ^bThin film, λ_{fl} = fluorescence maximum, λ_{ph} = phosphorescence maximum, ϕ = quantum yield, τ = fluorescence life time

tric constant and refractive index which are different in the solid state. A large red shift, as is the case for the cyanophenyl derivative, may suggest formation of excimer-like species.

Fluorescence lifetimes of 1–4 were measured in dichloromethane solution and in thin film by TCSPC technique.²³ The fluorescence decays were multiexponential (see Supporting Information) and the average lifetimes are reported in the table 1. Quantum yields were measured in solution^{24,25} were low (2–4%) for 1, 2 and 4. The quantum yield in thin films were calculated using lifetime ratios in solution and solid state, assuming constant radiative rate in the two media. The emission peaks, quantum yields, fluorescence lifetimes of 1–4 obtained in solution and in thin films are summarized in table 1.

The important energy levels of organic molecules in solid state for organic electronics are exciton levels (singlet and triplet excited state), transport levels (corresponding to cation and anion of the molecule) and exciton binding energy (excess energy required for exciton to give rise to a pair free cation/hole and anion/electron).^{26,27} These energy levels are determined for 1–4 as follows.

Optical band gap ($S_0 - S_1$) of 1–4 is usually determined from the transition energy at the intersection of the normalized emission and excitation spectra in thin films. This method is not suitable for 1–4 because of the large Stokes shift. Thus, the transition energy at the rising edge (10% of the peak value) of the fluorescence spectra was used to calculate the singlet energy ($S_0 - S_1$) level. A similar method was used to determine triplet ($S_0 - T_1$) level using the

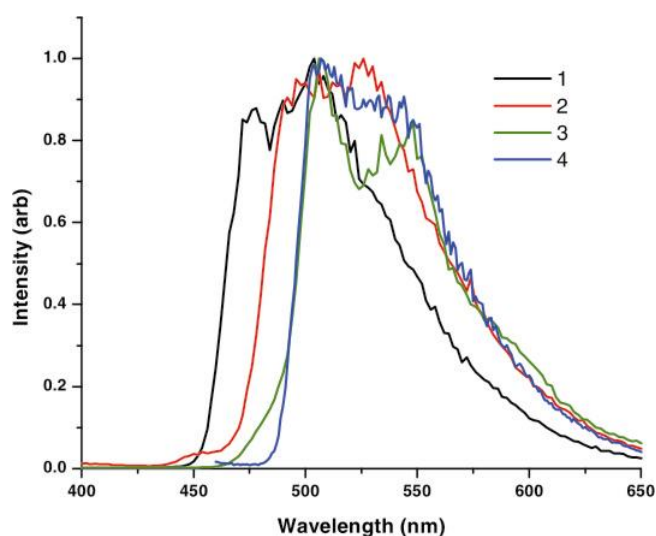
phosphorescence spectra. Phosphorescence emission spectra of 1–4 (figure 4) were recorded in powder samples using flash lamp ($\lambda_{ex} = 300$ nm for 1–2 and 360 nm for 3–4) with a delay time of 100 μ s and integrated time of 2 s at 77 K. A red shift in phosphorescence emission is observed for 1–4 (table 1). $S_0 - T_1$ gap for 1–4 is in the range of 2.51–2.70 eV.

Cyclic voltammetric oxidation and reduction potentials provide information on the HOMO and LUMO levels of the molecules, which in solid state are the transport levels for the hole and electron, respectively. The linear correlation of electrochemical oxidation and reduction potential of organic molecules determined in solvent like dichloromethane with the ionization potential and electron affinity of the molecules in solid state is well established.²⁸ Thus, E_{HOMO} is calculated by using Ep_{ox} ,^{28,29} $E_{HOMO} \approx -Ep_{ox}$ (vs Ferrocene) – 4.8 eV. Cyclic voltammetry of 1–4 in dichloromethane (conc. [1–4] ~ 1 mM, tetrabutyl ammonium hexafluorophosphate 0.1 M as supporting electrolyte) showed irreversible oxidation indicating that cation radical is unstable in dichloromethane. The peak potential was determined versus ferrocene as internal standard. 1–4 were not reducible in the electrochemical range accessible in dichloromethane. In the absence of cyclic voltammetric reduction, E_{LUMO} cannot be calculated directly. However, the transport gap, namely, the gap between E_{HOMO} and E_{LUMO} is greater than $S_0 - S_1$ gap by an amount equal to binding energy (BE) which is nearly zero only for large conjugated molecules.³⁰ Table 2 shows the values of Ep_{ox} , E_{HOMO} and ($E_{LUMO} - BE$) for 1–4.

Table 2. Electrochemical data and energy levels of 1–4.

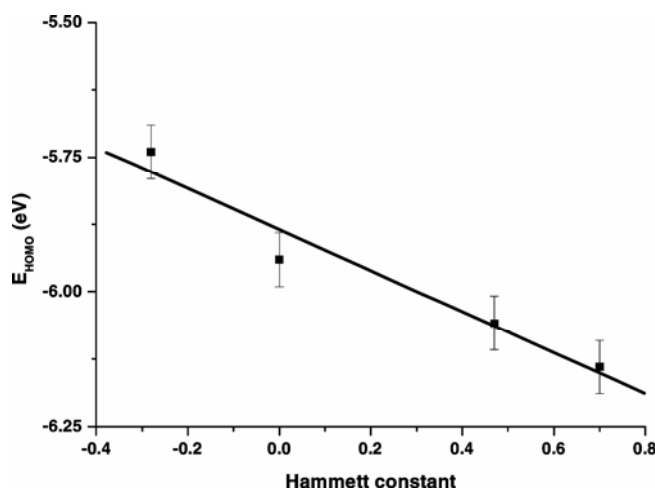
Compounds	$E_{p_{\text{ox}}}$ (V) ^a	E_{HOMO} (eV)	$E_{\text{LUMO}} - \text{BE}$ (eV)
1	1.14	-5.94	-2.45
2	0.94	-5.74	-2.34
3	1.34	-6.14	-2.91
4	1.25	-6.05	-2.80

^avs ferrocene, $E_{\text{HOMO}} = -(E_{p_{\text{ox}}} \text{ (vs ferrocene)} + 4.8) \text{ eV}$,
 $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{S0-S1}} + \text{BE}$

**Figure 4.** Phosphorescence spectra of 1–4 in powder sample at 77 K.

Theoretical study of 2,8-diphenyl-dibenzothiophene, 1 was carried out by density functional theory (DFT) calculations using Gaussian 03.³¹ This calculation provided an insight on the distribution of the HOMO densities at different positions in the molecule (See Supporting Information). It shows that *ortho* and *para* positions of phenyl group contribute to the HOMO. Hence, the substitution at *ortho* and *para* position of the phenyl group with electron withdrawing/donating groups should tune the HOMO energy level. Experimentally determined $E_{p_{\text{ox}}}$ (E_{HOMO}) vary substantially for 1–4. A linear relationship E_{HOMO} with Hammett constant of the substituent in 1–4 (figure 5) is observed, which is in agreement with the linear free energy relation of the Hammett constant.³²

The usefulness of 1–4 in organic electronics is now discussed. As emission layer in OLED 3 may be useful because of the higher quantum yield (~12% in thin film) and absence of self quenching. The deep

**Figure 5.** Correlation of E_{HOMO} of 1–4 with Hammett constant.

HOMO levels suggest that 1–4 will be suitable as good hole blocking material if ITO/TPD anode is used for hole injection. 1–4 are phosphorescent with triplet energy in the range of 2.5–2.7 eV, and thus suitable as host material for harvesting triplets in OLEDs to increase the internal efficiency,³³ even 100%, by using energy compatible, guest phosphor dopants of high quantum yield.

4. Conclusions

In conclusion, we have synthesized and characterized a series of 2,8-diphenyldibenzothiophene derivatives having different substituents in the phenyl group. The photophysical properties of these compounds showed that the substitution of phenyl groups at the *para* position causes red shift in absorption, fluorescence and phosphorescence. HOMO, LUMO levels, singlet and triplet energies were calculated from the experimental data.

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Supporting information

¹H, ¹³C NMR spectra, emission spectra in solution, life time data in dichloromethane and in thin films, cyclic voltammograms of 1–4 and Gaussian calculation for dibenzothiophene are provided. See www.ias.ac.in/chemsci for supporting information.

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