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Poly(naphthylenethiophene)s and poly(naphthylenevinylenephenylenevinylene)s: effect of naphthalene positional isomers on the light emitting properties of their polymers

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Abstract

Poly(naphthylenethiophene)s and poly(naphthylenevinylene-phenylenevinylene)s prepared from 1,5-dibromo-3,7-di-*t*-butylnaphthalene showed a significant blue shift in their UV–vis and photoluminescence spectra compared to copolymers derived from the 1,4-naphthylene system, both in solution and in thin film. This is correlated to a change in conjugation effect of the two positional isomers of naphthalene in the polymer backbone, where in 1,4-conjugation an aromatic sextet remains intact in one of the naphthalene rings whereas 1,5-conjugation involves the loss of resonance energy in the entire naphthalene unit. The series of poly(naphthylenevinylene-phenylvinylene)s emitted blue-green light with very high fluorescence quantum yields (80–95%) in solution. A fabricated device showed external quantum efficiency estimated at 0.2–0.4%, with a relatively high turn-on voltage at ~7.0 V.

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Keywords: Copolymers; Light emission; Positional isomers

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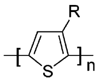
1. Introduction

The dynamic development in advanced materials research has led to the study of many organic conjugated polymers with varied light-emitting properties [1]. Homopolymers of poly(3-alkylthiophene)s of general structure **1** (PT), for example, exhibit good red color purity but tend to have rather low fluorescence quantum yields [2]. After the electroluminescent properties of the first poly(phenylenevinylene) (PPV) was demonstrated [1a], the family of PPVs derived from the general structure **2** is now among the most extensively studied organic light emitting materials covering a wide range of emitting colors. Copolymers containing at least two different conjugated segments are expected to exhibit novel electronic, optoelectronic and optical properties that are not found in the individual homopolymers [3]. A recent report on the diblock copolymer **3** [4], for example, showed that it exhibits very different thermal, electrochemical and morphological properties compared to PT or PPV oligomers.



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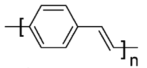

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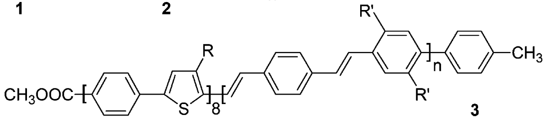

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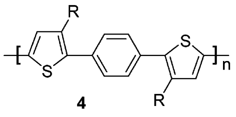

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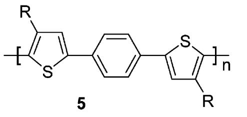

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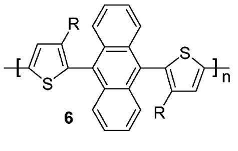

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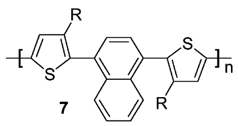

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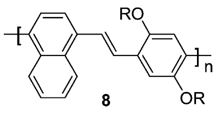

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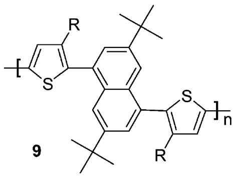

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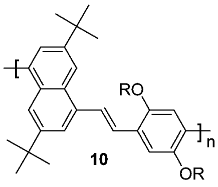

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Examples of homo or copolymers incorporating higher benzenoids in the polymer backbone are few. The parent phenylenethiophene series **4** was first reported by Chan and Ng [5]. More recently we have reported the photoluminescent properties of the phenylene [6], anthracene [6b] and naphthylene–thiophene [7] copolymers **5**–**7**. Examples of poly(naphthalenes)s reported earlier [8], however, suffered from the shortcomings of structural irregularity and insolubility in organic solvents. On the basis of the structure-property theory, the electronic properties of the conjugated polymers are highly dependent on both the nature of the active building blocks and the way in which they are linked [9]. The naphthalene unit could in principle be linked in the copolymer backbone in three different ways to allow a quinoid character [10] in conjugation: through their 1,4-, 1,5-, or 2,6-positions, respectively. To date several 1,4- and 2,6-naphthylenevinylene copolymers and derivatives have been studied for their optical properties [11]. Only limited examples of copolymers involving 1,5-conjugated naphthalene derivatives had been reported [12]. In addition, very little of their chemistry was investigated and essentially no details of their physical properties was described. Using 1,5-dibromo-2,7-di-*t*-butylnaphthalene as a synthetic precursor, we describe a systematic comparative study of the effects of incorporating the 1,5-napthalene units into the polymer backbone of poly(naphthylenethiophene) and poly(naphthylenevinylenephenhylenevinylene) copolymers. A blue shift in their light emitting properties was clearly observed going from the 1,4-naphthalene series of **7** and **8** to the 1,5-naphthalene series **9** and **10**, respectively.

2. Experimental

2.1. Characterization

^{1}H NMR (300 MHz) and ^{1}C NMR (75.5 MHz) data were recorded on a Bruker DPX 300 FT-NMR spectrophotometer. $CDCl_3$ was the solvent used and chemical shift was expressed relative to Me_4Si as an internal standard. EIMS spectra were obtained with a Micromass 7034E mass spectrometer using an ion current of 70 eV. FT-IR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr discs for solid samples and between KBr salt plates for liquid samples. Ultraviolet–visible (UV–vis) and fluorescence spectra were obtained using a Shimadzu UV 3101 PC UV–Vis-NIR spectrophotometer and a Perkin–Elmer LS 50B luminescence spectrometer with a xenon lamp as light source, respectively. Elemental analyses were conducted at the Chemical and Molecular Analysis Center, Department of Chemistry, National University of Singapore, on a Perkin–Elmer 240C elemental analyzer. Thermogravimetric analyses were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 20 °C/min from 20 to 800 °C and a nitrogen flow rate of 70 cm^3/min. GPC measurements were carried out on a Waters 2690 Separation Module equipped with a Waters 410 differential refractometer HPLC system and Waters Styragel HR3, HR4 and HR5 columns in series using polystyrene as a standard and HPLC grade THF as eluent.

2.1.1. *1,4-Bis[2-(3-n-octylthienyl)]naphthalene* (**15c**)

A solution of 1,4-dibromonaphthalene (2.86 g, 10 mmol) and 2-tri-*n*-butylstannyl-3-*n*-octylthiophene (24.25 g, 50 mmol) in DMF (60 ml) was carefully degassed by three freeze-thaw cycles and the catalyst $Pd(PPh_3)_4$ (0.069 g, 0.06 mmol) was added. After the mixture was heated at 120 °C for 3 days, the solvent was removed under vacuum. The product was dissolved in diethyl ether and the resulting solution was washed with aqueous 0.5 M KF, water, brine and was dried over sodium sulfate. The solvent was evaporated off and the residue was purified by chromatography (silica gel, hexane as eluant) to give **15c** as colorless oil (3.0 g, 77%). ^{1}H NMR: δ 7.85–7.82 (m, 2H), 7.53 (s, 2H), 7.48–7.45 (m, 2H), 7.39 (d, $J = 5.2$ Hz, 2H), 7.10 (d, $J = 5.2$ Hz, 2H), 2.44 (t, $J = 7.6$ Hz, 4H), 1.56–1.51 (m, 4H), 1.33–1.16 (m, 20H), 0.87 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR: δ 140.93, 134.94, 133.15, 132.51, 128.34, 128.34, 126.42, 126.06, 124.41, 31.72, 30.42, 29.17, 29.12, 29.06, 28.68, 22.54, 13.99. Anal. $C_{34}H_{44}S_2$: calcd C 79.01, H 8.58; found C 78.95, H 8.49. MS (EI, *m/z*): 516 (M^+).

2.2. *General procedure for the preparation of* **16**

A solution of **12** (10 mmol) and **13** (50 mmol) in DMF (60 ml) was carefully degassed by three freeze thaw cycles and the catalyst $Pd(PPh_3)_4$ (0.06 mmol) was added. After the mixture was heated at 120 °C for 3 d, the solvent was removed under vacuum. The product was dissolved in diethyl ether and the resulting solution was washed with aqueous 0.5 M KF, water and brine and was dried over sodium sulfate. The solvent was removed under reduced pressure. The product was obtained from repeated recrystallization from ethanol.

2.2.1. *1,5-Bis[2-(3-n-butylthienyl)]-3,7-di-t-butylnaphthalene (**16a**)*

This was isolated as white solid (80%). ^{1}H NMR: δ 7.76 (d, $J = 2.0$ Hz, 2H), 7.58 (d, $J = 2.0$ Hz, 2H), 7.40 (d, $J = 5.2$ Hz, 2H,), 7.12 (d, $J = 5.2$ Hz, 2H), 2.47 (t, $J = 7.6$ Hz, 4H), 1.60–1.47 (m, 4H), 1.36 (s, 18H), 1.26–1.18 (m, 4H), 0.76 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR: δ 147.04, 140.53, 136.09, 131.63, 131.31, 128.32, 128.15, 124.13, 121.45, 34.76, 32.75, 31.11, 28.44, 22.21, 13.69. Anal. $C_{34}H_{44}S_2$: calcd C 79.01, H 8.58; found C 78.85, H 8.39. MS (EI, *m/z*): 516 (M$^+$).

2.2.2. *1,5-Bis[2-(3-n-octylthienyl)]-3,7-di-t-butylnaphthalene (**16c**)*

This was isolated as white solid (77%). ^{1}H NMR: δ 7.70 (d, $J = 2.0$ Hz, 2H), 7.52 (d, $J = 2.0$ Hz, 2H), 7.36 (d, $J = 5.2$ Hz, 2H), 7.08 (d, $J = 5.2$ Hz, 2H,), 2.42 (t, $J = 7.6$ Hz, 4H), 1.53–1.46 (m, 4H), 1.31 (s, 18H), 1.25–1.07 (m, 20H), 0.83 (t, $J = 6.8$ Hz, 6H,). ^{13}C NMR: δ 146.98, 140.51, 136.04, 131.54, 131.23, 128.29, 128.08, 124.08, 121.38, 34.72, 31.70, 31.07, 30.59, 29.25, 29.14, 29.03, 28.73, 22.47, 13.94. Anal. $C_{42}H_{60}S_2$: calcd C 80.19, H 9.61; found C 80.01, H 9.49. MS (EI, *m/z*): 628 (M$^+$).

2.2.3. *1,5-Bis[2-(3-n-dodecylthienyl)]-3,7-di-t-butylnaphthalene (**16e**)*

This was isolated as white solid (79%). ^{1}H NMR: δ 7.70 (d, $J = 2.0$ Hz, 2H), 7.52 (d, $J = 2.0$ Hz, 2H), 7.36 (d, $J = 5.2$ Hz, 2H), 7.08 (d, $J = 5.2$ Hz, 2H), 2.40 (t, $J = 7.6$ Hz, 4H), 1.54–1.48 (m, 4H), 1.30 (s, 18H), 1.27–1.12 (m, 36H), 0.87 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR: δ 146.98, 140.51, 136.02, 131.54, 131.23, 128.29, 128.06, 124.06, 121.36, 34.72, 31.80, 31.07, 30.62, 29.51, 29.41, 29.32, 29.22, 29.17, 28.74, 22.56, 13.98. Anal. $C_{50}H_{76}S_2$: calcd C 81.01, H 10.33; found C 79.89, H 10.06. MS (EI, *m/z*): 740 (M$^+$).

2.3. *General procedure for the preparation of copolymers **7** and **9***

A solution of **15** or **16** (3.5 mmol) in dry chloroform was added dropwise to a stirred solution of anhydrous ferric chloride (2.27 g, 14 mmol) in dry chloroform at 0 °C. The mixture was stirred for 4 h at 0 °C with a slowly dynamic flow of nitrogen and then the reaction was allowed to further proceed at room temperature for another 24 h. The obtained dark solution was diluted with chloroform and then dedoped by 50% aqueous hydrazine hydrate overnight. The obtained brown solution was washed with water until the aqueous layer is colorless. The mixture was poured into stirred methanol to precipitate the polymer. The brown solid was filtered and then washed with acetone using a Soxhlet apparatus. The soluble fractions of the polymer were extracted with chloroform by Soxhlet extraction and re-precipitated in methanol, insoluble dark solid residue was observed in the Soxhlet extractor in all cases.

2.3.1. *Poly{1,4-bis[2-(3-n-octylthienyl)]naphthalene} (**7c**)*

This was isolated as a dark brown solid (60%). ^{1}H NMR: δ 7.90–7.42 (br, 6H), 7.17–6.97 (br, 2H), 2.52–2.47 (br, 4H), 1.54–1.24 (br, 24H), 0.82–0.73 (br, 6H). FT-IR (cm^{-1}): 3072, 3044, 2950, 2922, 2851, 1576, 1505, 1455, 1376, 838, 763, 720. Anal. $(C_{17}H_{21}S)_n$: calcd C 79.38, H 8.17, S 12.45; found C 77.83, H 7.35, S 11.69.

2.3.2. *Poly{1,5-bis[2-(3-n-butylthienyl)]-3,7-di-t-butylnaphthalene} (**9a**)*

This was isolated as a dark brown solid (60%). ^{1}H NMR: δ 7.95–7.48 (br, 4H), 7.27–7.09 (br, 2H), 2.51–2.45 (br, 4H), 1.59–1.29 (br, 26H), 0.84–0.71 (br, 6H). FT-IR (cm^{-1}): 3060, 2954, 2924, 2853, 1601, 1462, 1375, 1233, 884, 835, 711. Anal. $(C_{17}H_{21}S)_n$: calcd C 79.38, H 8.17, S 12.45; found C 77.83, H 7.35, S 11.69.

2.3.3. *Poly{1,5-bis[2-(3-n-octylthienyl)]-3,7-di-t-butylnaphthalene} (**9c**)*

This was isolated as a dark brown solid (57%). ^{1}H NMR: δ 7.90–7.42 (br, 4H), 7.20–7.09 (br, 2H), 2.50–2.42 (br, 4H), 1.49–1.19 (br, 42H), 0.86–0.74 (br, 6H). FT-IR (cm^{-1}): 3062, 2956, 2924, 2854, 1597, 1461, 1376, 1234, 884, 705. Anal. $(C_{21}H_{29}S)_n$: calcd C 80.51, H 9.27, S 10.22; found C 71.98, H 7.89, S 9.02.

2.3.4. *Poly{1,5-bis[2-(3-n-dodecylthienyl)]-3,7-di-t-butylnaphthalene} (**9e**)*

This was isolated as a dark brown solid (54%). ^{1}H NMR: δ 7.93–7.41 (br, 4H), 7.21–7.08 (br, 2H), 2.53–2.40 (br, 4H), 1.83–1.26 (br, 58H), 0.82–0.72 (br, 6H). FT-IR (cm^{-1}): 3060, 2924, 2853, 1598, 1463, 1368, 1241, 884, 720. Anal. $(C_{25}H_{37}S)_n$: calcd C 81.30, H 10.03, S 8.67; found C 77.74, H 8.93, S 7.18.

2.4. *General procedure for the preparation of copolymers **8** and **10***

A solution of **11** or **12** (1 mmol), **14** (1 mmol), palladium acetate (0.04 mmol), tri-*o*-tolylphosphine (0.2 mmol), tri-*n*-butylamine (0.5 ml) in DMF (10 ml) was heated at reflux under nitrogen for 48 h. A yellow-green suspension resulted. The mixture was poured into methanol (200 ml) and the yellow-green precipitate collected by filtration. The product was purified further by dissolving in a small amount of THF and re-precipitating by adding the THF solution dropwise into methanol. The resulting solid was washed with methanol, acetone and then extracted by chloroform in a Soxhlet extractor. The desired polymer was isolated after removal of chloroform under reduced pressure. The polymer was further dried under vacuum.

2.4.1. *Poly(2,5-di-n-hexyloxy-1,4-phenylenevinylene-1,4-naphthylenevinylene) (**8b**)*

This was isolated as a red powder (82%). FT-IR (KBr, cm^{-1}): 3044, 2925, 1600, 1497, 1465, 1381, 1198, 1025, 958, 841, 747, 503. Anal. $(C_{32}H_{38}O_2)_n$: calcd C 84.54, H 8.42; found C 83.26, H 8.44.

2.4.2. Poly(2,5-di-n-hexyloxy-1,4-phenylenevinylene-3,7-di-t-butyl-1,5-naphthylenevinylene) (10b)

This was isolated as an intensely fluorescent yellow-green powder (43%). FT-IR (KBr, cm^{-1}): 3049, 3014, 2964, 2934, 1595, 1469, 1378, 1199, 1021, 958, 876, 687, 524. Anal. $(C_{40}H_{54}O_2)_n$: calcd C 84.75, H 9.60; found C 84.37, H 9.72.

2.4.3. Poly(2,5-di-n-decyloxy-1,4-phenylenevinylene-3,7-di-t-butyl-1,5-naphthylenevinylene) (10d)

This was isolated as an intensely fluorescent yellow-green powder (51%). FT-IR (KBr, cm^{-1}): 2926, 1597, 1468, 1383, 1203, 1038, 958, 876, 689, 520. Anal. $(C_{48}H_{70}O_2)_n$: calcd C 84.90, H 10.39; found C 83.15, H 10.39.

2.4.4. Poly(2,5-di-n-tetradecyloxy-1,4-phenylenevinylene-3,7-di-t-butyl-1,5-naphthylenevinylene) (10f)

This was isolated as an intensely fluorescent yellow-green powder (46%). FT-IR (KBr, cm^{-1}): 2925, 1597, 1467, 1384, 1203, 1033, 958, 877, 709, 493. Anal. $(C_{56}H_{86}O_2)_n$: calcd C 85.00, H 10.95; found C 83.92, H 11.20.

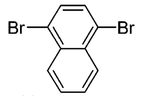
2.5. LED device

Polymer **10b** was dissolved in chloroform and filtered through a 0.45 μm PTFE filter. Patterned indium tin oxide (ITO) coated glass substrates were cleaned with acetone, methanol, detergent and distilled water sequentially in an ultrasonic bath. After treatment with oxygen plasma, 1500 Å of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P 4083, Bayer AG) was spin-coated onto the substrate followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of the polymer **10b** was coated onto the anode by spin casting inside a drybox. The film thickness of the active layer was around 80–100 nm. A 20 nm thick calcium film covered with a 200 nm thick silver cathode were deposited by thermal evaporation. Device performance was measured inside a drybox. Current-voltage ($I-V$) characteristics were recorded with a Keithley 236 source meter. Luminance and external quantum efficiencies were determined by a calibrated photodiode.

3. Results and discussion

3.1. Synthesis and characterization

Treatment of naphthalene with dioxane dibromide resulted mainly in 1,4-bromination to give dibromonaphthalene **11** [13]. Although *t*-butylation of naphthalene gave a mixture of the 2,6- and 2,7-di-*t*-butyl isomers [14] the former could be isolated by repeated co-crystallization with thiourea. Subsequent selective bromination governed by steric demand led to the formation of 1,5-dibromo-3,7-di-*t*-butylnaphthalene **12** [15]. The series of 2-tri-*n*-butylstannyl-3-alkylthiophenes [16] **13a**, **13c** and **13e** and that of 1,4-dialkoxy-2,5-divinylbenzenes [17] **14b**, **14d** and **14f** were prepared according to procedures reported in the literature.



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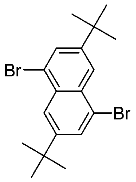

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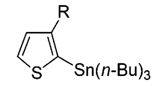

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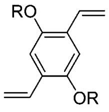
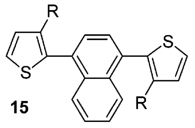


14

	R
a	n-C_4H_9
b	n-C_6H_{13}
c	n-C_8H_{17}
d	n-$C_{10}H_{21}$
e	n-$C_{12}H_{25}$
f	n-$C_{14}H_{29}$



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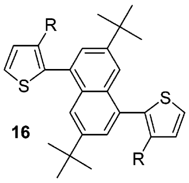

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A palladium-catalyzed [16] coupling reaction between **11** and **13c** afforded the monomer **15c**. Similar reactions between **12** and the corresponding **13** gave the series of monomers **16a**, **16c** and **16e**, respectively. The yield of monomers depended significantly on the conditions of the cross-coupling reaction. The optimized conditions involved the use of 6×10^{-3} equiv. of $Pd(PPh_3)_4$ as the catalyst with the reaction performed in DMF maintained at a temperature of about 120 °C. The monomers **15** and **16** were isolated in 75–80% yield after purification. Polymerization of the monomers was performed through ferric chloride oxidation in anhydrous chloroform [18]. The polymers were dedoped by treatment with ammonium hydroxide. As the polymers were insoluble in water, an aqueous ammonium hydroxide solution was added slowly to a solution of the polymer in THF. The dedoping process was shown to be essentially complete by XPS studies where no band corresponding to Fe was observed in the spectra of the polymer samples. After the dedoping process, the solids were isolated by filtration. The sample was then washed with acetone and extracted with chloroform using a Soxhet system. The poly(naphthylenethiophene) copolymers **7c**, **9a**, **9c** and **9e** were obtained as yellow solids in about 70% yield. The molecular weights of these copolymers were determined by means of gel permeation chromatography (GPC) using THF as an eluant and polystyrene as the standard. Their respective number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity indices are outlined in Table 1. This series of polymers have low molecular weights accounting for their relatively high

Table 1
General properties of the copolymers **7**–**10**

Polymer	GPC results			Thermal analysis	
	M_n	M_w	PDI	TGA T_d (°C)	DSC T_g (°C)
7c	4520	6320	1.3	434	32
9a	4840	8620	1.7	402	37
9c	5010	19,030	3.8	430	–[a]
9e	5310	11,110	2.0	401	–[a]
8b	29,900	58,100	1.9	404	72
10b	27,200	45,600	1.7	411	83
10d	20,000	39,200	2.0	402	39
10f	20,400	42,100	2.1	422	–[a]

[a] Not noticeable.

solubility in common organic solvents such as chloroform, THF, toluene and xylenes.

The poly(naphthylenevinylenephenylenevinylene) copolymers **8b**, **10b**, **10d** and **10f** were synthesized via Heck coupling reactions between **11** or **12** and the corresponding monomers **14** [17,19]. Optimum yields of 40–50% of the copolymers **10** could only be obtained when the reactions were carried out for 48 h at solvent (DMF) refluxing temperature at about 160 °C. Due to the high reaction temperature employed, the higher boiling tri-*n*-butylamine was used to replace triethylamine as a base to prevent loss of the base during the long reaction time. Under similar conditions, copolymer **8b** was isolated in about 80% yield. A reason for the slower and less satisfactory polymerization to give **10** might be indirectly due to the steric demand of the *t*-butyl groups on the naphthalene ring. The desired copolymers **8** and **10** were isolated as red and yellow-green powders, respectively, indicating a very different conjugation effect going from a 1,4- to a 1,5-naphthalene unit. In comparison to copolymers **7** and **9** mentioned earlier, the molecular weights of **8** and **10** were found to be significantly higher (Table 1). However, the copolymers **8** and **10** still exhibited high solubility in chloroform, THF, toluene and xylenes.

The experimental and calculated values are in good agreement (see Section 2) for the elemental contents in the copolymers **7**–**10**, demonstrating that in general the molecular structures of the copolymers are as expected. In addition there are specific spectroscopic data supporting the key structural features in the copolymers. Going from the FT-IR spectrum of monomer **16a** to that of copolymer **9a** (Fig. 1(a)), it is evident that the vibration associated with thiophene's α C–H stretch has essentially vanished while the vibration attributed to the thiophene β C–H stretch is unchanged. This indicates that the oxidative polymerization occurred extensively at the terminal α sites on the thiophene, yielding the desired fully conjugated polymer **9**. The divinyl monomer **14b** shows two absorption signals at 900 and 995 cm^{-1} (CH=CH_2 out-of-plane deforming mode) in its FT-IR spectrum (Fig. 1(b)). These are, however, absent in the spectrum of the copolymers **10b** while two new absorption signals appear at 1596 (*trans* CH=CH stretching mode) and 960 cm^{-1} (*trans* CH=CH out-of-plane deforming mode). This is clearly consistent with the formation of the *trans*-disubstituted vinylene group in the copolymers **10** [20].

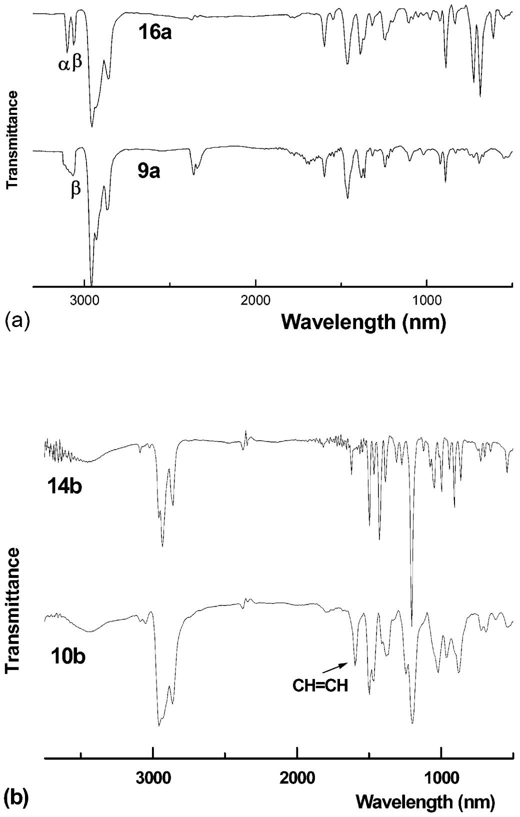


Fig. 1. FT-IR spectra of (a) **16a** and **9a**, and (b) **14b** and **10b**.

A comparison between the ^{13}C NMR spectra of the monomer **16a** and its corresponding copolymer **9a** indicates a new and significant resonance appearing in the spectrum of **9a** at about 147 ppm (Fig. 2). This is expected of the coupling of two thiophene α C–H units of two separate monomers to form the thiophene–thiophene C–C bond in the polymer. Fig. 3 shows a representative comparison of

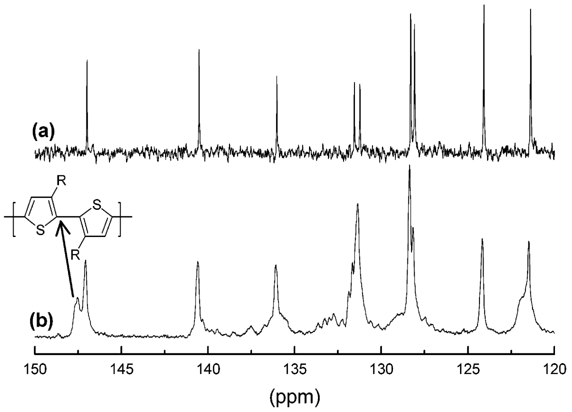


Fig. 2. ^{13}C NMR spectra of aromatic carbons in (a) monomer **16a** and (b) copolymer **9a**.

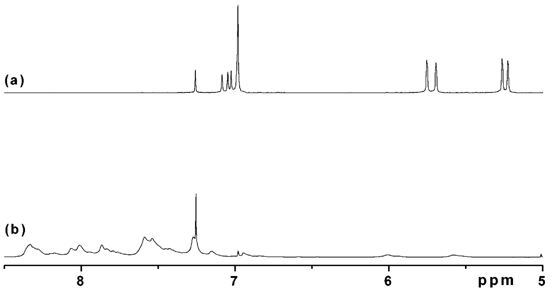


Fig. 3. ^{1}H NMR spectra of aromatic and vinylic protons in (a) monomer **14b** and (b) copolymer **8b**.

the ^{1}H NMR spectra of divinyl monomer **14b** and the corresponding polymer **8b**. The olefinic protons in **14b** was clearly observed as two doublets in the range of δ 5.2–5.8. In the spectrum of **8b** only very weak signals were still observed in the range of δ 5.5–6.0 indicating a low presence of terminal olefinic protons. This is consistent with a favorable polymerization between **11** and **14b** to produce polymer **8b** with relatively high molecular weights.

3.2. Thermal analysis

The thermal analyses of the copolymers **7–10** were performed in a nitrogen environment and the data obtained are summarized in Table 1. All copolymers in general exhibited an onset of degradation temperature greater than 400 °C with 5% weight loss indicative of good thermal stability. About 20–30% residue was left after the temperature was raised to 800 °C because of the non-decomposed polymer backbone. From DSC studies, the series of polymers **7** and **9** in general showed low or unnoticeable glass transition temperatures (T_g) (Table 1). On the contrary, polymers **8b** and **10b** exhibited reasonably high T_g at 70–80 °C. An increase in the length of substituted chains is expected to induce a steady decrease in T_g and this was clearly observed going from **10b** to **10d** to **10f** (Table 1).

3.3. Optical properties

The optical/spectroscopic properties of copolymers **7–10** were measured both in solution (THF) and in thin film. The UV–visible absorption (UV–vis) spectra and photoluminescence (PL) spectra of all the polymers in THF solution (ca. 1×10^{-5} M) and in thin film are shown in Figs. 4–6, respectively. Their optical data (UV–vis absorption and PL) are outlined in Table 2. The films were spin-cast onto quartz plates from their solutions in xylene (2% w/V). All the films prepared were visibly uniform and emit bright fluorescence with colors ranging from red, bluish green to blue. Generally, the absorption spectra of the series **9a**, **9c** and **9e**, and those of **10b**, **10d** and **10f**, respectively, do not exhibit noticeable changes with varying chain length in the dialky groups.

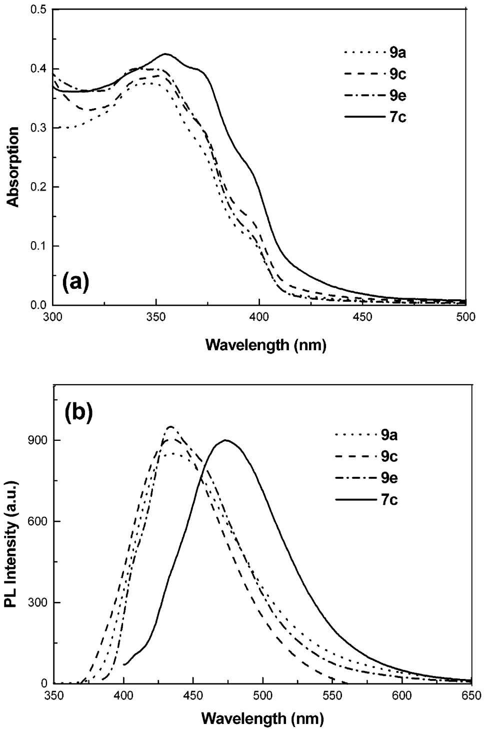


Fig. 4. (a) UV–vis absorption and (b) photoluminescence spectra of **7c**, **9a**, **9c** and **9e** in THF solutions (~ 1×10^{-5} M).

In solution, going from polymer **7** to **9** indicated a blue-shift in the absorption UV–vis absorption (Fig. 4(a)) with the spectra of **9a**, **9c** and **9d** being almost identical. In their corresponding photoluminescence (PL) spectra (Fig. 4(b)), a significant blue-shift of about 40 nm

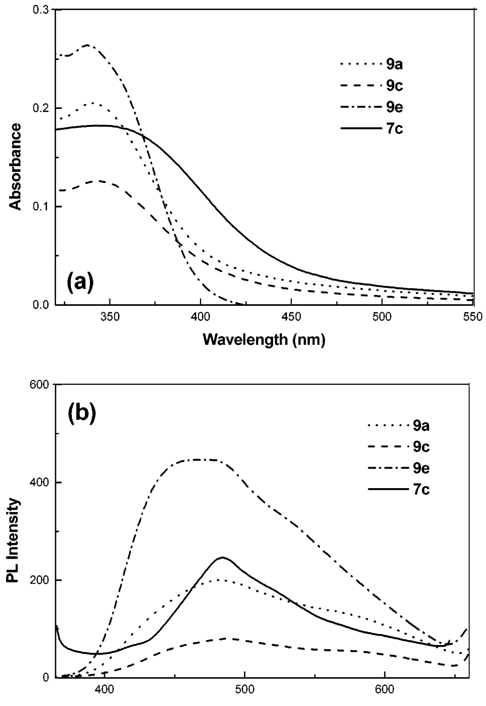


Fig. 5. (a) UV–vis absorption and (b) photoluminescence spectra of **7c**, **9a**, **9c** and **9e** measured from their spin-coated films on quartz plates at room temperature.

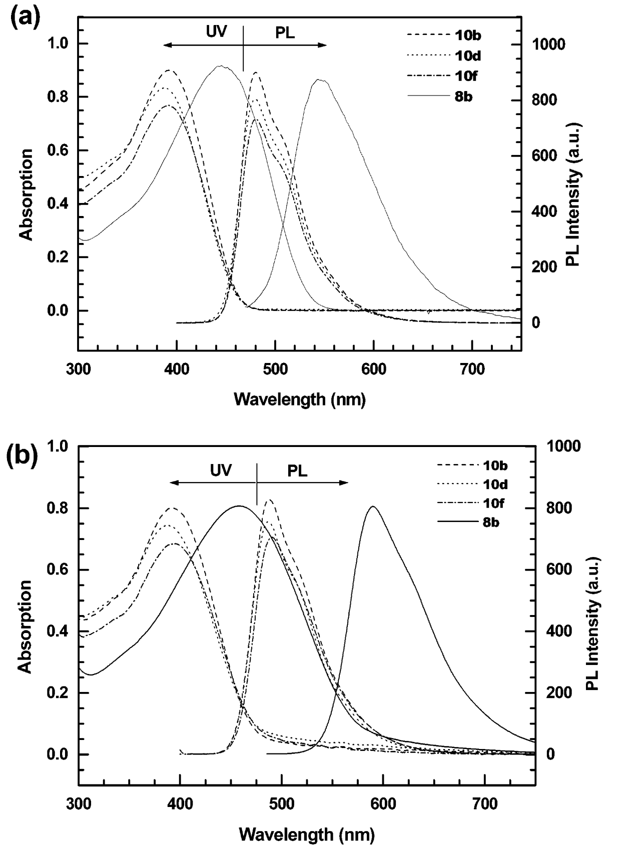


Fig. 6. UV–vis absorption and photoluminescence spectra of **8b**, **10b**, **10d** and **10f** in (a) THF solutions and (b) in solid film states at room temperature.

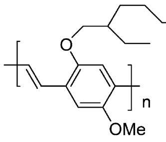
(Table 2) was clearly evident. The almost identical spectra of **9a**, **9c** and **9d** suggest that the preferred conformations of the dialkyl chains in the polymer series were alike in solution. At least there was no discernable effect of chain length on the effective conjugation for the polymers being observed. In thin film, bands in both the UV–vis and PL spectra of **7** and **9** were significantly broader and less intense (Fig. 5), and the blue-shift was relatively less obvious (Table 2). The spectra for the series of polymers **8** and **10** were, however, significantly better resolved (Fig. 6). The blue shift going from **8b** to the series of polymers **10** was clearly observed in both their UV–vis and PL spectra in solution with shifts of about 55 and 65 nm (22.54 and 19.07 eV), respectively (Table 2). In thin film, this effect was even more pronounced with shifts of about 65 and 100 nm (19.07 and 12.40 eV), respectively, observed in their UV–vis and PL spectra (Table 2). Thus among the series of copolymers **7**–**10** a wide range of emitting colors was observed in solution: from red for **8b**, to bluish-green for **7c** and **10**, to blue for **9**. In thin film, **8** still exhibited red emission while the series of copolymers **7**, **9** and **10** all served as bluish-green emitter. The appreciable PL red shift going from solution to thin film may be due to a better conjugation along the polymer main chain in the solid state, or the intrachain and/or interchain interactions generated in the solid state of the polymer.

Table 2
Optical properties of the copolymers **7**–**10**

Polymer	λ_{max} (THF), nm (eV)		λ_{max} (films), nm (eV)		E_g [a] (eV)	Φ_{FL} [b] (%)
	abs	em	abs	em		
7c	354 (3.50)	473 (2.62)	342 (3.63)	484 (2.56)	2.80	32
9a	347 (3.57)	435 (2.85)	340 (3.65)	481 (2.58)	3.06	35
9c	351 (3.53)	434 (2.86)	342 (3.63)	486 (2.55)	3.00	33
9e	341 (3.64)	433 (2.86)	337 (3.68)	474 (2.62)	3.14	27
8b	446 (2.66)	544 (2.78)	458 (2.71)	590 (2.10)	2.06	1
10b	392 (3.16)	478 (2.59)	392 (3.16)	487 (2.55)	2.55	95
10d	388 (3.16)	476 (2.60)	388 (3.16)	486 (2.55)	2.55	83
10f	392 (3.16)	477 (2.60)	395 (3.14)	491 (2.53)	2.55	91

[a] E_g is the band gap energy estimated from the onset wavelength of the optical absorption.
[b] In THF solution.

The fluorescence quantum yields (Φ_{FL}) of the polymers **7**–**10** in their THF solutions were estimated by quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4, having the fluorescence quantum yield of 55%) as the standard [21] and the results are given in Table 2. There was no significant change in Φ_{FL} among the poly(naphthylenethiophene)s going from the 1,4-**7c** to the 1,5-**9**. It was, however, surprising to note that while the 1,4-**8b** was essentially 'non-fluorescent' the series of 1,5-**10** exhibited very high fluorescence quantum yields (80–95%). This effect may be in part attributed to the 1,5-substituted naphthalene moieties contributing to a more rigid polymer structure with the effect that relaxation from the excited state through a non-radiative (e.g. thermal) process will be reduced with consequently higher fluorescence quantum yield [22]. There is, however, no simple explanation for the large difference in Φ_{FL} going from **8** to **10**.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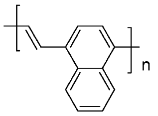
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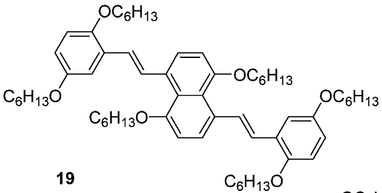
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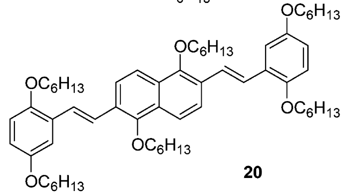
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Among reported examples of poly(arylenethiophene)s having similar '1,4-links', going from the phenylene system

Table 3
A comparison of optical properties of representative copolymers **7**–**10** and related oligomers or polymers reported in the literature

Properties	**9a**	**7c**	**4c** [5a]	**6b** [6b]	**10b**	**8b**	**17** [23]	**18** [11c]	**19** [9]	**20** [9]
$\mathrm{UV}_{\mathrm{film}}$ $\lambda_{\max}$, nm (eV)	347 (3.57)	354 (3.50)	420 (2.95)	406 (3.05)	392 (3.16)	458 (2.71)	526 (2.36)	450 (2.76)	373 (3.32)	388 (3.20)
$\mathrm{PL}_{\mathrm{film}}$ $\lambda_{\max}$, nm (eV)	435 (2.85)	473 (2.62)	521 (2.38)	477 (2.60)	487 (2.55)	590 (2.10)	590 (2.10)	580 (2.14)	468 (2.65)	545 (2.27)

4c [5a] to the naphthylene **7c** or anthracene **6b** [6b] resulted in a similar but significant blue shift in their $\mathrm{PL}_{\mathrm{film}}$ $\lambda_{\max}$ (Table 3) corresponding to red emission for **4c** and green for **6b** and **7c**. Changing the 1,4-link in **7c** to the 1,5-link in **9a**, however, did not lead to significant changes in their $\mathrm{PL}_{\max}$ $\lambda_{\max}$. It was indicated earlier that the emission maximum of a thin film of polymer **8b** was observed at 590 nm (absorption maximum at 458 nm). The emission value is in fact identical to that observed for a typical PPV derivative such as MEH-PPV **17** (Table 3) [23]. This indicates that the conjugation behavior of 1,4-naphthalene ring in **8b** is similar to that in a benzene ring in PPVs (Fig. 7). The polymer **10b**, however, exhibits a significant blue shift in emission light to 487 nm. This should mainly be due to the interruption of conjugated length along the polymer backbone in going from the 1,4- to the 1,5-naphthalene system (Fig. 7), where in 1,4-conjugation an aromatic sextet remains intact whereas 1,5-conjugation involves the loss of resonance energy in the entire naphthalene unit. The disruption in both the naphthalene rings in **10b** (and **10d**, **10f**) is expected to result in an appreciably larger bandgap (Table 2) compared to that of **8b** which is consistent with the observed blue shift in emission.

Compared to the properties of **8b**, the polymer series **10** exhibit very significantly higher PL efficiency in addition to their large blue shift in solid state photoluminescence (Table 2). Efficient blue-green light emission, good solubility in common organic solvents, good thermal stability and good film-forming properties of the 1,5-napthalene series make them promising candidates as models to study emissive materials in light-emitting diodes. The blue shift in emission going from **8b** to **10b** could qualitatively be compared with the pair of poly(1,4-naphthalene vinylene) **18** and the 1,5-naphthalene vinylene trimer **19** (Table 3). Emission maximum of the former was observed at 580 nm taken under an excitation of 450 nm [11c]; the absorption of the later was at about 373 nm with an emission maximum at 468 nm [9]. Going from the trimer **19** to trimer **20** [9] results in a further blue shift (about 80 nm; Table 3) of emission light. This suggests that a sequential blue shift of emission color going from a 1,4-napthalene conjugation (such as **18**) to a 2,6-naphthalene conjugation (such as **20**) to a 1,5-napthalene conjugation (such as **19**). Taking note that **19** and **20** are trimers, our observation on the properties in going from polymeric **8** to polymer series **10** has provided complementary evidence that polymerization at different pair of sites on the naphthalene moiety could be used as a means to tune the color of the emitting light (or other optical properties) of the polymers.

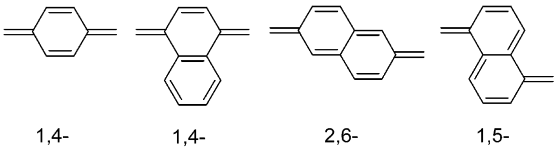
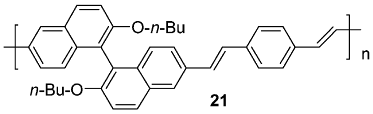


Fig. 7. Quinoid structures of benzene and naphthalene.



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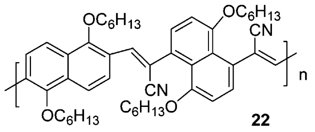

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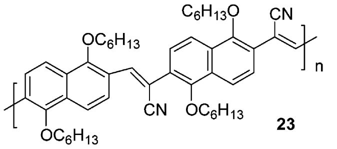

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Among the reported naphthalene-containing PPV derivatives a selected list of examples, namely polymers **21** [24], **22** [9] and **23** [11a], are used to compare with the properties obtained for **10b** in our work (Table 4). In general the polymer **10b** is superior in one or more aspects than any of the other polymers in their desired properties. Polymer **21** has a very high polydispersity index suggesting varied polymer chain lengths. Its emission light falls only in the green region while that of **10** has a bluish intensity. In comparison to polymer **22** which also exhibits blue-green emission, **10b** forms polymers of significantly higher molecular weights. **10b** holds a similar advantage over polymer **23**. In addition, the emission spectrum of **23** shows a shoulder at 526 nm resulting in a relatively broad signal width. Thus in conclusion polymer **10b** exhibits collectively more desirable optical properties compared to those of

Table 4
A comparison of selected properties among a list of naphthalene-containing PPV derivatives

Properties	**10b**	**21** [24]	**22** [9]	**23** [11a]
$M_w \times 10^4$	4.56	2.43	0.31	1.70
$M_n \times 10^4$	2.72	0.58	0.23	0.71
Polydispersity	1.67	4.20	1.33	2.40
$\mathrm{UV}_{\mathrm{film}}$ $\lambda_{\max}$ (nm)	392	395	402	427
$\mathrm{FL}_{\mathrm{film}}$ $\lambda_{\max}$ (nm)	487	525	499	499 (526)

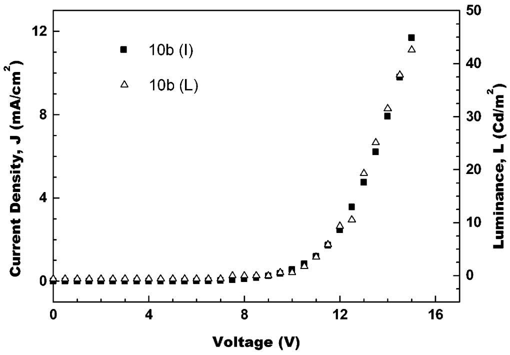

Fig. 8. Current density–voltage–brightness relationship. For the device ITO/PEDOT/**10b**/Ca/Al.

reported systems hence offers a better model as blue-green light emitting organic polymer.

3.4. Electroluminescence properties

A LED device ITO/PEDOT/polymer/Ca/Ag was fabricated with polymer **10b** to examine the EL properties. Qualitatively the device from polymer **10b** still gave bluish-green emission at about 490 nm following the trace of its PL spectrum. Turn-on voltage for the device of **10b** was, however, found to be relatively high at ~7.0 V (Fig. 8). Despite its very high fluorescence quantum yield at 95% in solution, the external quantum efficiency of the device was estimated to be 0.2–0.4% for **10b**. These results were, however, reproducible in three separate devices made from **10b**.

Acknowledgements

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