

Control of π -Stacking for Highly Emissive Poly(*p*-phenylenevinylene)s: Synthesis and Photoluminescence of New Tricyclodecane Substituted Bulky Poly(*p*-phenylenevinylene)s and Its Copolymers

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Received: November 11, 2005; In Final Form: December 14, 2005

In the present work, we have demonstrated a facile approach to increase the luminescence of the poly (*p*-phenylenevinylene)s via controlling the molecular aggregates induced by π -stacking. We have synthesized new bulky tricyclodecane (TCD) substituted PPVs: poly(2-methoxy-5-tricyclodecanemethyleneoxy-1,4-phenylenevinylene) (**MTCD-PPV**), poly(bis-2,5-tricyclodecanemethyleneoxy-1,4-phenylenevinylene) (**BTCD-PPV**), and a series of symmetrically substituted bulky PPV copolymers (**P-1–P-7**) covering the entire composition range from 0 to 100 mol %. The structures of the monomers and polymers were confirmed by ^1H NMR and FTIR, and the molecular weights were determined by gel permeation chromatography. The composition analysis by NMR revealed that the bulky monomer was highly reactive and the incorporation of bulky units in **MEH-PPV** increased irrespective of the feed ratio. The polymers possess good solubility, high molecular weights, good thermal stability, and so forth. The molecular weights of the PPV copolymers were also significantly affected by the bulky substitution: the higher the incorporation of bulky units, the lower the molecular weight. The absorption and emission studies revealed that there was no influence on the **MEH-PPV** by TCD substitution in solution whereas in the solid state the photoluminescence intensity of PPV increased more than 10 times. The luminescence increase in PPV was observed throughout the entire bulk and was not confined to any particular domain in the polymer. The bulky PPV copolymers showed that both the luminescence intensity (in film) and quantum yields (in solution) increased with an increase in the extent of BTCD incorporation in the **MEH-PPV** and attained a maximum for 50% BTCD. The TCD unit has thus proved to be an efficient bulky substituent for PPV as it controls the π -stack-induced molecular aggregates in the polymer chains by increasing the interchain distances. The new bulky PPV copolymers are highly soluble, thermally stable, and highly luminescent besides being economically cheap compared to the other materials reported so far for the bulkier approach in π -conjugated materials.

Introduction

Controlling of molecular aggregates in π -conjugated polymer chains is an important field of research to improve their performance in optoelectronic devices such as organic light-emitting diodes (LEDs).¹ In electronic devices, small organic emitters are found to be superior in luminescence properties compared to polymeric emitters mainly because they have less of a preference toward molecular aggregation compared to the latter.² Since the emissive species in the conjugated polymers are restricted due to chain rigidity, they have a tendency to undergo aggregation via π -stacking, more particularly in the solid state.^{3–6} This results in the formation of weakly emissive interchain species in the excited state and reduces the luminescence efficiency, which restricts the use of polymeric emitters in devices, despite their good mechanical properties and easy processability compared to small organic emitters.^{7,8} Among the approaches attempted to control the molecular aggregation in π -conjugated polymers, the confinement of conjugation length and increasing interchain polymer distances are worth mentioning.¹ The confinement in conjugation length was normally achieved by introducing either nonconjugated aliphatic units or

molecular kinks based on 1–3 aromatic meta linkages.^{9–16} The confinement route was successful in addressing several interesting questions relating to exciton migration, primary processes of photoexcitation, energy transfer, photoluminescence and electroluminescence efficiency, and so forth.⁹ However, one of the limitations of this approach is that the HOMO–LUMO energies of the confined structures are different from that of the parent polymer, which often causes difficulty in choosing the work function of electrodes and also alters the color of emission.¹⁷ On the other hand, the separation of interchain distances using suitable anchoring groups is attractive because the aggregation can be controlled without altering the HOMO–LUMO levels.

Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)s (**MEH-PPV**) and its copolymers are one of the most thoroughly studied π -conjugated polymers because of their potential applications in polymer LEDs and plastic solar cells.¹⁸ Recently, various research groups have reported the synthesis of PPVs containing substituents such as cyclohexyl,^{19–21} cyclohexylmethylene,^{22,23} adamantaneethylene,^{24–26} cholestanyl,^{27,28} naphthyl,²⁹ quinoxaline,³⁰ oligomeric silsesquioxane,^{31,32} and cationic phenyl group³³ for controlling the molecular aggregation in the solid state. Among the various bulky PPVs, the polymers containing the cyclohexylmethylene and adaman-

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taneethylene groups were reported to be very efficient in increasing the luminescence intensity by 4–5 times. However, the adamantane and cholestanyl–PPVs were not soluble in common solvents, which limits the complete structural characterization and its processability in electronic devices.^{24,27} The photoluminescence properties of cyclohexylmethylene/MEH-PPV copolymers were found irrational over the composition, and more detailed studies are required for a better understanding.²³ Additionally, the cyclohexylmethylene and adamantane-ethylene derivatives are very expensive, and their high raw material cost makes this approach less attractive especially for large-scale applications in LEDs. Meijer et al. investigated the oligo-phenylenevinylene (OPV) units attached in the poly-(propylene imine) dendritic structures and reported that the dendrite structure separated the OPV units for an increase in their luminescence intensity.³⁴ Bao et al. reported the gallic acid derivative based dendritic liquid crystalline PPVs, and they suggested that dendritic PPVs may not be ideal for single-layer devices since they contain a large number of insulating side groups.^{35–37} Therefore, developing low cost and highly luminescent new bulky PPVs through easy synthetic routes (similar to MEH-PPV) from commercially available low-cost material is an attractive and essential requirement for futuristic applications, in general, for the bulky π -conjugates. Additionally, a few important fundamental questions such as (i) the minimum amount of bulky substituents required for maximum luminescence efficiency (i.e., composition effect), (ii) the effect of bulky substituents on the polymerization and the resultant molecular weights, (iii) the effect of bulky units on the three-dimensional (3D) ordering of polymer chains, and (iv) the role of bulky substituents on the solubility, photo- and thermal stability, and so forth, are very important and will be addressed.

In the search for new derivatives or substituents for the synthesis of highly emissive freely soluble PPVs to address the above-mentioned issues, we have come across a new rigid cycloaliphatic alcohol, tricyclodecanemethanol (TCD). TCD is a very attractive bulky anchoring group for π -conjugated polymers because of its tricyclic rigid bulky structure; also, it is sluggish to crystallize, has low cost, and has commercial availability. TCD-based acrylics have recently been explored;³⁸ however, up to our knowledge, there are no reports of conducting polymers based on TCD in the literature. Here, as a first attempt based on TCD conducting polymers, we report novel tricyclodecane substituted bulky poly(phenylenevinylene)s: poly-(2-methoxy-5-tricyclodecanemethyleneoxy-1,4-phenylenevinylene) (MTCD-PPV), poly(bis-2,5-tricyclodecanemethyleneoxy-1,4-phenylenevinylene) (BTCD-PPV), and a series of copolymers containing bis-TCD substitution in MEH-PPV (P-1–P-7). The copolymer compositions are varied from 0 to 100 mol % to investigate the effect of bulky substituents on the emissive properties of MEH-PPV in the entire composition range. The role of the bulky TCD unit on the photoluminescence properties of PPV was investigated in both solution and the solid state to understand the molecular aggregation of this new bulky substituent to explore as a futuristic highly luminescent π -conjugated material.

Experimental Methods

Materials. 1,8-Tricyclodecanemethanol (TCD) was donated by Celanese Chemicals & Co. and used without further purification. *p*-Toluene sulfonyl chloride, 4-methoxyphenol, hydroquinone, 2-ethylhexylbromide, and potassium *tert*-butoxide were purchased from Aldrich Chemicals. HBr in glacial acetic

acid, paraformaldehyde, and all other reagents/solvents were purchased locally and purified by following the standard procedures.

General Procedures. ¹H and ¹³C NMR spectra of the compounds and polymers were recorded using a 300 MHz Bruker NMR spectrophotometer in CDCl₃, containing a small amount of TMS as the internal standard. IR spectra of the samples were recorded using a Nicolet Impact 400 D Fourier transform IR (FTIR) spectrophotometer in the solid state. An amount of 1–2 mg of the solid was mixed with KBr, and the spectrum was recorded from 4000 to 600 cm^{−1}. The purity of the monomers and intermediate compounds was determined by JEOL JSM600 fast atom bombardment (FAB) high-resolution mass spectrometry (HRMS). The compound was dissolved in CHCl₃ and suspended in 3-nitrobenzyl alcohol as a matrix for FAB mass measurements. Thermal analysis of the polymer was performed using a Rheometric Scientific DSC Plus instrument, and the instrument was calibrated with indium, tin, and lead standards. All samples were first heated to melt at 280 °C prior to recording their thermograms to remove their previous thermal history and recorded using a heating/cooling rate of 10 °C/min, under a 5 mL/min purge of dry nitrogen. The thermal stability of the polymers was determined using a TGA-50 Shimadzu thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen atmosphere. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using polystyrene as the standard. The flow rate of THF was maintained as 1 mL/min. The polymer solution was prepared by dissolving 3 mg of the sample in 1 mL of THF, then filtered and injected for recording the GPC chromatograms. The chromatograms are recorded using a Waters 510 pump and detectors of Waters 2487 UV–vis detector and a Waters 410 differential RI detector. Three mixed styrogel columns in series HT 6E, HR 5E, and HR 4E are employed for the separation. The absorption and emission studies were performed by a Perkin-Elmer Lambda 35 UV–vis spectrophotometer and a SPEX Fluorolog F112X spectrofluorimeter. For recording solid-state photophysical properties, thin films were cast from chloroform solution on a glass plate and allowed to dry for 24 h prior to measurements. The film thicknesses were varied by changing the concentration of the solution and speed of the homemade film casting setup. The fluorescence quantum yields of the polymer were determined in CHCl₃ using Rhodamine 6G in water ($\phi = 0.95$) as the standard by exciting at 480 nm. The concentration of the polymer solution and the standard was adjusted in such a way to obtain the absorbance equal to 0.1 at 480 nm. The quantum yields of the samples are calculated by following the reported procedure.³⁹

Synthesis of 1,8-Tricyclodecanemethylenetosylate (TCD-OTs). 1,8-Tricyclodecanemethanol (25.0 g, 0.15 mol) in 25 mL of pyridine was added to an ice-cold solution of *p*-toluene sulfonyl chloride (32.2 g, 0.17 mol) in 30 mL of dry pyridine. The solution was stirred for 8 h in an ice bath, and then it was slowly warmed to room temperature, and the stirring continued for an additional 12 h. It was then poured into ice-cold 50% HCl, extracted into diethyl ether, and dried over anhydrous Na₂SO₄. The solvent was evaporated to obtain the product as a viscous liquid, which turned into a white crystalline solid upon cooling. It was then purified by passing through a silica gel column using pet ether/chloroform (70:30 v/v) as the eluent. Yield = 41.4 g (86%). Mp = 50–52 °C. ¹H NMR (CDCl₃, δ): 7.81 ppm (d, 2H, Ar-H), 7.37 ppm (d, 2H, Ar-H), 3.84 ppm (m, 2H, −OCH₂), 2.45–0.79 ppm (m, 15H, cyclic-H). ¹³C

NMR (CDCl₃, δ): 144.4, 133.5, 129.7, 127.9 (**Ar-C**), 73.7 (**-OCH₂**), 45.4, 44.9, 43.3, 41.1, 39.9, 34.1, 28.8, 27.5, 26.8, 26.3, 21.6 ppm (**cyclic-C**). FTIR (KBr, cm⁻¹): 2925, 1600, 1508, 1458, 1366, 1229, 1178, 1101, 1027, 959, 831, 821, 666 cm⁻¹. HRMS (MW = 320.4): m/z = 339.2 (M⁺·H₂O).

Synthesis of 1-Methoxy-4-(1,8-tricyclodecanemethyleneoxy)-benzene (3). 4-Methoxyphenol (6.2 g, 0.05 mol) and powdered KOH (8.4 g, 0.15 mol) were taken in a 250 mL flask containing 50 mL of dry ethanol and refluxed under nitrogen atmosphere for 0.5 h. **TCD-OTs** (19.2 g, 0.06 mol) was added, and the reaction was continued by refluxing for 24 h under nitrogen atmosphere. It was cooled, poured into water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The solvent was evaporated to obtain the product as a light brown colored solid. It was further purified by passing through a silica gel column using 35% CH₂Cl₂ in petroleum ether as the eluent. Yield = 9.8 g (72%). Mp = 61–63 °C. ¹H NMR (CDCl₃, δ): 6.75 ppm (s, 4H, **Ar-H**), 3.92 ppm (s, 3H, **-OCH₃**), 3.69 ppm (m, 2H, **-OCH₂**), 2.37–0.89 ppm (m, 15H, **cyclic-H**). ¹³C NMR (CDCl₃, δ): 153.8, 153.7, 115.8, 114.8 (**Ar-C**), 73.2 (**Ar-OCH₃**), 55.9 (**Ar-OCH₂**), 45.8, 45.5, 44.0, 41.5, 40.4, 40.3, 34.7, 29.2, 28.2, 27.2, 26.7 ppm (**cyclic-C**). FTIR (KBr, cm⁻¹): 2937, 2871, 1859, 1639, 1509, 1468, 1449, 1386, 1286, 1237, 1174, 1107, 1033, 820 cm⁻¹. HRMS (MW = 272.4): m/z = 272.7 (M⁺).

Hydroquinone (2.0 g, 0.02 mol), powdered KOH (4.5 g, 0.08 mol), and **TCD-OTs** (12.7 g, 0.04 mol) were reacted to obtain 1,4-bis(1,8-tricyclodecanemethyleneoxy)benzene (**4**) by following the similar procedure described for **3**. Yield = 3.5 g (47%). Mp = 125–126 °C. ¹H NMR (CDCl₃, δ): 6.74 ppm (s, 2H, **Ar-H**), 3.64 ppm (m, 4H, **-OCH₂**), 2.34–0.88 ppm (m, 30H, **cyclic-H**). ¹³C NMR (CDCl₃, δ): 115.5 (**Ar-C**), 72.9 (**Ar-OCH₂**), 45.6, 45.2, 43.7, 41.3, 40.2, 34.5, 28.9, 28.0, 26.9, 26.4 ppm (**cyclic-C**). FTIR (KBr, cm⁻¹): 2945, 2863, 2357, 1643, 1505, 1464, 1382, 1282, 1226, 1103, 1044, 1025 cm⁻¹. HRMS (MW = 406.6): m/z = 407.1 (M⁺).

Synthesis of 1,4-Bis(bromomethyl)-2-methoxy-5-(1,8-tricyclodecanemethyleneoxy)benzene (5). Compound **3** (2.9 g, 0.01 mol) and paraformaldehyde (1.5 g, 0.05 mol) in 70 mL of glacial acetic acid were taken in a 250 mL two-neck flask. HBr in glacial acetic acid (5 mL, 30–33 wt %) was added dropwise to the above solution at 25 °C and stirred for 0.5 h under N₂ atmosphere. It was gradually heated to 80 °C and stirred for an additional 4 h. The brown colored reaction mixture was cooled and filtered, and the solid was washed with water until the filtrate was neutral. The solid was dissolved in 100 mL of chloroform and washed with NaHCO₃ solution and saturated brine solution. The organic layer was separated and dried over anhydrous Na₂SO₄, and the solvent was evaporated to obtain the product as a white crystalline solid. Yield = 2.0 g (42%). Mp = 98–99 °C. ¹H NMR (CDCl₃, δ): 6.79 ppm (s, 2H, **Ar-H**), 4.67 ppm (s, 4H, **-CH₂Br**), 3.79 ppm (s, 3H, **-OCH₃**), 3.73 ppm (m, 2H, **-OCH₂**), 2.38–0.95 ppm (m, 15H, **cyclic-H**). ¹³C NMR (CDCl₃, δ): 151.0, 127.5, 114.7, 113.6 (**Ar-C**), 72.8 (**Ar-OCH₃**), 56.2 (**Ar-OCH₂**), 45.6, 45.2, 43.8, 41.3, 40.2, 34.6, 28.9, 28.7, 28.6, 27.9, 26.9, 26.5 ppm (**cyclic-C**). FTIR (KBr, cm⁻¹): 2945, 2363, 2331, 1558, 1508, 1410, 1316, 1231, 1202, 1033, 862 cm⁻¹. HRMS (MW = 458.2): m/z = 458.8 (M⁺).

Compound **4** (5.0 g, 0.01 mol) and paraformaldehyde (1.9 g, 0.06 mol) in 100 mL of glacial acetic acid were treated with HBr in glacial acetic (7 mL, 30–33 wt %) acid as described for **5** to prepare white crystalline 1,4-bis(bromomethyl)-2,5-di(1,8-tricyclodecanemethyleneoxy)benzene (**6**). Yield = 6.4 g

(86%). Mp = 135–136 °C. ¹H NMR (CDCl₃, δ): 6.84 ppm (s, 2H, aromatic), 4.53 ppm (s, 4H, **-CH₂Br**), 3.81 ppm (m, 4H, **-OCH₂**), 2.44–1.03 ppm (m, 30H, **cyclic-H**). ¹³C NMR (CDCl₃, δ): 127.5, 114.7 (**Ar-C**), 72.9 (**Ar-OCH₂**), 45.6, 45.2, 43.8, 41.3, 40.3, 34.6, 29.0, 28.7, 27.9, 27.0, 26.5 ppm (**cyclic-C**). FTIR (KBr, cm⁻¹): 2946, 2355, 1560, 1505, 1469, 1408, 1315, 1230, 1205, 1031, 905, 869, 756, 687 cm⁻¹. HRMS (MW = 592.5): m/z = 593.1 (M⁺).

Synthesis of 1-Methoxy-4-(2-ethylhexyloxy)benzene (7). 4-Methoxyphenol (6.2 g, 0.05 mol) and powdered KOH (11.2 g, 0.20 mol) were taken in a 250 mL flask containing 50 mL of distilled DMSO and heated under nitrogen atmosphere for 0.5 h. 2-Ethylhexyl bromide (10.7 mL, 0.06 mol) was added and heated at 80 °C for 36 h under nitrogen atmosphere. It was cooled and poured into excess water and extracted into dichloromethane. The organic layer was washed with NaOH followed by brine solution and dried over anhydrous Na₂SO₄, and the solvent was evaporated. The crude product was further purified by passing through a silica gel column using 35% CH₂Cl₂ in petroleum ether as the eluent. Yield = 8.0 g (67%). ¹H NMR (CDCl₃, δ): 6.86 ppm (s, 4H, **Ar-H**), 3.83 ppm (m, 5H, **-OCH₂** and **-OCH₃**), 2.61–0.94 ppm (m, 20H, **aliphatic-H**). ¹³C NMR (CDCl₃, δ): 115.6 (**Ar-C**), 71.4 (**Ar-OCH₂**), 55.8, 39.7, 30.7, 29.3, 24.0, 23.3, 14.3, 11.3 ppm. FTIR (KBr, cm⁻¹): 2964, 2930, 2874, 2830, 1591, 1505, 1460, 1438, 1379, 1282, 1226, 1174, 1100, 1040 cm⁻¹.

Hydroquinone (3.0 g, 0.027 mol) and powdered KOH (12.1 g, 0.22 mol) were reacted with 2-ethylhexyl bromide (11.5 mL, 0.07 mol) as described for **7** to obtain 1,4-bis(2-ethylhexyloxy)benzene (**8**). Yield = 6.2 g (68%). ¹H NMR (CDCl₃, δ): 6.86 ppm (s, 4H, **Ar-H**), 3.83 ppm (s, 4H, **-OCH₂**), 1.76–0.94 ppm (m, 30H, **aliphatic-H**). ¹³C NMR (CDCl₃, δ): 115.6 (**Ar-C**), 71.4 (**Ar-OCH₂**), 39.7, 30.8, 29.3, 24.1, 23.3, 14.3, 11.3 ppm (**aliphatic-C**). FTIR (KBr, cm⁻¹): 2960, 2930, 2874, 2365, 1840, 1587, 1505, 1460, 1379, 1222, 1100, 1036, 928 cm⁻¹.

Synthesis of 1,4-Bis(bromomethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene (9). Compound **7** (3.0 g, 0.01 mol) and paraformaldehyde (1.9 g, 0.06 mol) in 40 mL of glacial acetic acid was reacted with HBr in glacial acetic acid (7 mL, 30–33 wt %) as described for **5** to obtain **9**. Yield = 4.9 g (91%). ¹H NMR (CDCl₃, δ): 6.87 ppm (s, 2H, **Ar-H**), 4.54 ppm (s, 4H, **-CH₂Br**), 3.89 ppm (d, 5H, **-OCH₂** and **-OCH₃**), 1.64–0.92 ppm (m, 15H, **aliphatic-H**). FTIR (KBr, cm⁻¹): 2958, 2928, 1730, 1512, 1463, 1435, 1408, 1316, 1231, 1205, 1105, 1038, 895, 872, 758, 719, 681, 668 cm⁻¹.

Compound **8** (3.3 g, 0.01 mol) and paraformaldehyde (1.5 g, 0.05 mol) in 40 mL of glacial acetic acid were reacted with HBr in glacial acetic acid (5 mL, 30–33 wt %) as described for **5** to obtain 1,4-bis(bromomethyl)-2,5-di(2-ethylhexyloxy)benzene (**10**). Yield = 3.8 g (71%). ¹H NMR (CDCl₃, δ): 6.86 ppm (s, 2H, **Ar-H**), 4.53 ppm (s, 4H, **-CH₂Br**), 3.89 ppm (d, 5H, **-OCH₂** and **-OCH₃**), 1.75–0.92 ppm (m, 30H, **aliphatic-H**). FTIR (KBr, cm⁻¹): 2959, 2923, 2874, 2083, 1640, 1502, 1457, 1408, 1309, 1220, 1202, 1037, 952, 692 cm⁻¹.

Synthesis of Homo Poly(*p*-phenylenevinylene)s and Copolymers. The polymerization procedure for poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (**MEH-PPV**) and all other homopolymers and copolymers is the same. Compound **9** (0.43 g, 0.001 mol) (for MEH-PPV) was dissolved in dry THF (50 mL), and potassium *tert*-butoxide (6 mL in 1 M THF) was added to the solution and stirred well under nitrogen atmosphere for 24 h at 30 °C. The red precipitate obtained was poured into methanol, filtered, and washed successively with methanol and acetone. It was dried in a vacuum oven at 40 °C

TABLE 1: Molecular Weights, Compositions, and Degradation Temperature of the Polymers

polymer	BTCD in feed (mol %)	BTCD in copolymer (mol %) ^a	M_p^c (g/mol)	M_n^c (g/mol)	M_w^c (g/mol)	M_w/M_n	n^f	T_D^g (°C)
MEH-PPV	homo	homo	1,80,800	47,600	1,61,500	3.4	183	322
BEH-PPV	homo	homo	42,500	15,100	42,600	2.8	42	297
MTCD-PPV	homo	homo	5,700 ^d	5,200 ^d	12,400 ^d	2.4	18	302
BTCD-PPV	homo	100.0	^e					290
P-1	5	17.5 ^b	28 800	19 200	41 200	2.2	45	289
P-2	10	23.2 ^b	36 500	19 900	61 800	3.1	46	284
P-3	15	29.0	33 500	15 400	51 000	3.3	36	310
P-4	20	31.7	47 000	25 500	71 300	2.8	59	366
P-5	35	53.2	30 800	18 700	59 200	3.2	44	287
P-6	50	60.8	13 200	4600	15 000	3.2	11	303
P-7	63	75.0	8900	5900	17 500	2.9	14	290

^a Determined by ¹H NMR by comparing the intensities of peaks at 3.50 and 3.41 ppm as shown in Figure 1. ^b Calculated by extra-plotting the straight line fit as shown in Figure 2. ^c Molecular weights are determined by GPC in THF at 30 °C using polystyrene as the standard. ^d Partially soluble in THF at 30 °C for molecular weight determination. ^e Insoluble in THF for molecular weight determination. ^f Calculated number average degree of polymerization. ^g Degradation temperature at 10 wt % loss.

for 5 h prior to further analysis. Yield = 0.16 g (51%). ¹H NMR (CDCl₃, δ): 7.46 ppm (b, 2H, Ar-H), 7.13 ppm (s, 2H, CH=CH), 3.89 ppm (s, 5H, -OCH₃ and -OCH₂-), 1.55–0.85 ppm (m, 15H, aliphatic). FTIR (KBr, cm⁻¹): 3063, 2958, 2862, 1502, 1461, 1416, 1350, 1256, 1206, 1039, 964, 859, 779, 704 cm⁻¹.

Similarly, the monomers **5**, **6**, and **10** are polymerized using potassium *tert*-butoxide to obtain the polymers poly(2-methoxy-5-tricyclodecanemethyleneoxy-1,4-phenylenevinylene) (MTCD-PPV), poly(bis-2,5-tricyclodecanemethyleneoxy-1,4-phenylenevinylene) (BTCD-PPV), and poly(bis-2,5-ethylhexyloxy-1,4-phenylenevinylene) (BEH-PPV). The yield and molecular weights of the polymers are summarized in Table 1.

MTCD-PPV. Yield = 51%. ¹H NMR (CDCl₃, δ): 7.45 ppm (b, 2H, Ar-H), 7.11 ppm (s, 2H, CH=CH), 3.89 ppm (b, 3H, -OCH₃), 3.42 ppm (b, 3H, -OCH₂), 2.37–0.80 ppm (m, 15H, cyclic). FTIR (KBr, cm⁻¹): 3264, 2949, 2862, 1608, 1502, 1409, 1351, 1314, 1252, 1201, 1040, 968, 866, 780, 698, 619 cm⁻¹.

BTCD-PPV. Yield = 57%. ¹H NMR (CDCl₃, δ): 7.52 ppm (b, 2H, Ar-H), 6.52 ppm (b, 2H, CH=CH), 3.65 ppm (b, 4H, -OCH₂-), 2.88–0.87 ppm (m, 30H, cyclic). FTIR (KBr, cm⁻¹): 3045, 2949, 2862, 1611, 1598, 1499, 1415, 1348, 1250, 1199, 1028, 972, 863, 762 cm⁻¹.

BEH-PPV. Yield = 32%. ¹H NMR (CDCl₃, δ): 7.46 ppm (b, 2H, Ar-H), 7.13 ppm (s, 2H, CH=CH), 3.88 ppm (b, 4H, -OCH₂-), 1.75–0.83 ppm (m, 30H, aliphatic). FTIR (KBr, cm⁻¹): 3063, 2949, 2871, 1508, 1463, 1418, 1346, 1248, 1198, 1036, 967, 858, 773 cm⁻¹.

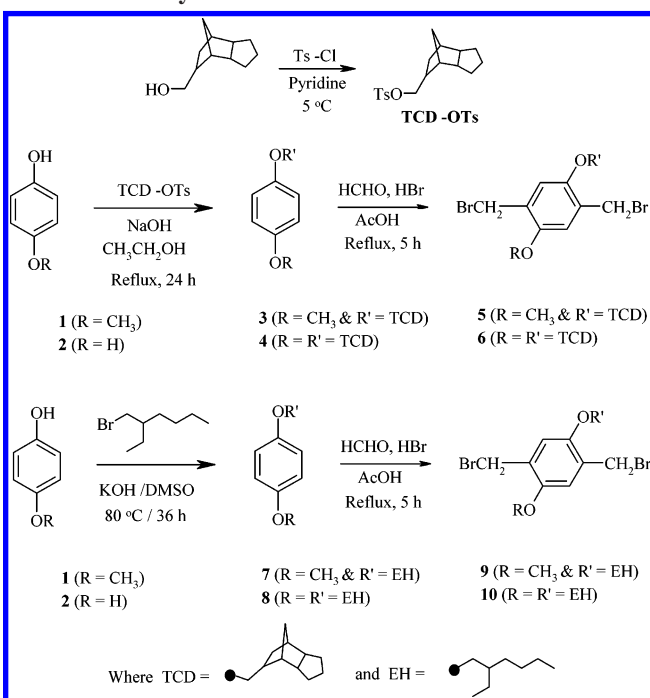
The PPV copolymers **P-1**–**P-7** were prepared by varying the amount of monomers **9** and **6** in the feed and following the similar procedure described for MEH-PPV. The composition in the feed and molecular weights are summarized in Table 1. The yields of the copolymers obtained are typically in the range of 35–52%.

P-6. ¹H NMR (CDCl₃, δ): 7.09 ppm (s, 2H, Ar-H), 6.75 ppm (s, 2H, CH=CH), 3.50 ppm (b, 5H, -OCH₃ + -OCH₂ (MEH)), 3.40 ppm (b, 4H, -OCH₂ (TCD)), 2.44–0.46 ppm (m, 15H, cyclic). FTIR (KBr, cm⁻¹): 3256, 3063, 2949, 2862, 1593, 1505, 1421, 1345, 1314, 1247, 1201, 1038, 973, 860, 771, 706, 619, 519 cm⁻¹. The ¹H NMR and FTIR spectra data for all other copolymers are similar to **P-6** except the differences in the peak intensities.

Results and Discussion

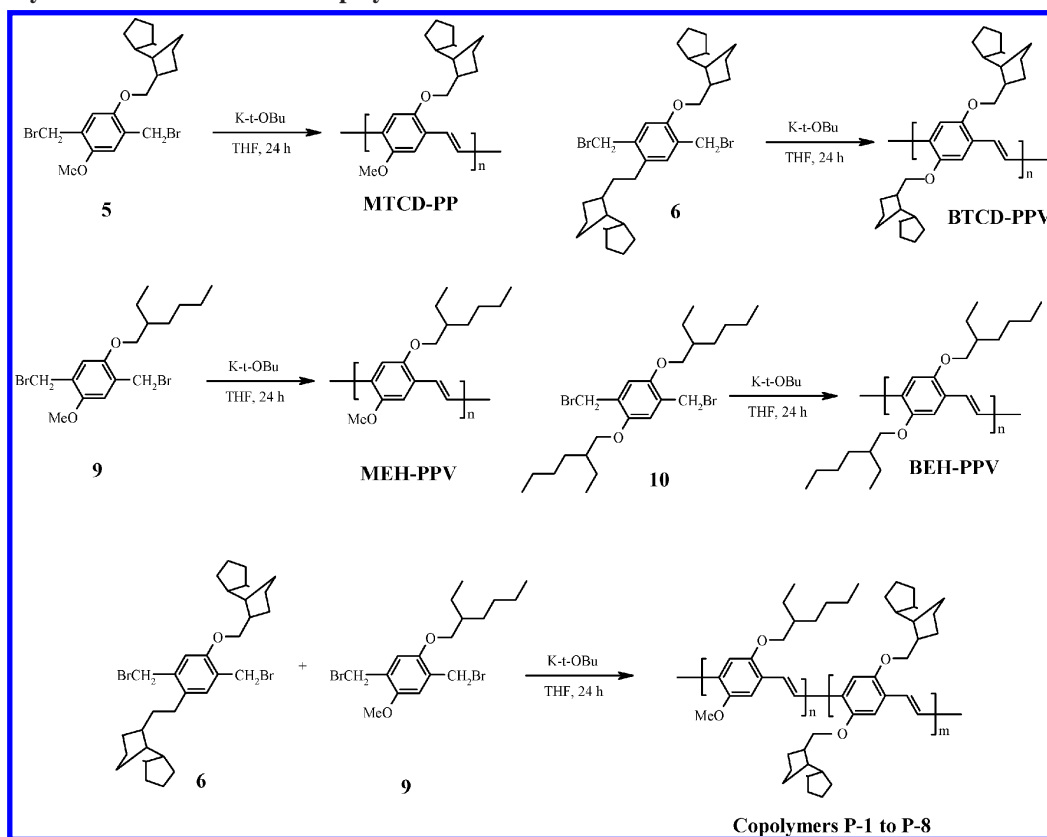
The synthesis of the monomers and polymers are shown in Schemes 1 and 2, respectively. TCD (from Celanese Chemicals) was reacted with *p*-toluene sulfonyl chloride in pyridine at ice-

SCHEME 1: Synthesis of New Monomers Based on TCD



cold conditions to convert it into the corresponding tricyclodecanemethylenetosylate (TCD-OTs). It was further reacted with 4-methoxyphenol (**1**) and hydroquinone (**2**) in NaOH/ethanol to produce 1-methoxy-4-tricyclodecanemethyleneoxybenzene (**3**) and bis-1,4-tricyclodecanemethyleneoxybenzene (**4**), respectively. Compounds **3** and **4** were heated in HBr/acetic acid in the presence of paraformaldehyde to yield the following bis-bromomethylated compounds: 1,4-bis-bromomethyl-2-methoxy-5-tricyclodecanemethyleneoxybenzene (**5**) and 1,4-bis-bromomethyl-2,5-tricyclodecanemethyleneoxybenzene (**6**), respectively. The monomers and the intermediate compounds were characterized by NMR, FTIR, and FAB-HRMS techniques. Compounds **5** and **6** were polymerized using potassium-*tert*-butoxide as a catalyst in dry THF for 24 h at ambient conditions under nitrogen atmosphere to produce polymers MTCD-PPV and BTCD-PPV, respectively (see Scheme 2). The other two monomers **9** and **10** were prepared as shown in Scheme 1 and polymerized to yield MEH-PPV and BEH-PPV, respectively. All the polymers were purified by pouring the red polymer solution into methanol, filtering, and subsequently washing with hot methanol and acetone. The purification procedure was repeated at least twice by dissolving and reprecipitating the

SCHEME 2: Synthesis of PPVs and Its Copolymers



polymer into methanol to remove the oligomers and other impurities. **MTCD-PPV** and **BTCD-PPV** were freely soluble in high boiling solvents such as 1,2-dichlorobenzene, but they were not completely soluble in common organic solvents such as chloroform and THF. **BTCD** unit containing **MEH-PPV** copolymers (**P-1–P-9**) were synthesized by varying the molar ratio of the monomers **6** and **9** in the feed as 5, 10, 15, 20, 35, 50, 63, 75, and 90 mol %. The higher incorporation of **BTCD** content (more than 75%) in **MEH-PPV** resulted in poor solubility of the copolymers, and therefore, in the present investigation, only **P-1–P-7** was taken for further analysis (see Scheme 2).

The structures of the polymers were confirmed by ^1H NMR and FTIR. The ^1H NMR spectra of **MEH-PPV**, **P-4**, **P-6**, and **MTCD-PPV** are shown in Figure 1. In all four spectra, the two aromatic peaks at 7.39 and 7.11 ppm correspond to the phenyl aromatic protons and vinyne ($\text{CH}=\text{CH}$) protons, respectively. The peaks for all other protons appeared below 4.00 ppm. The peaks for the end groups are essentially absent, and the intensities of all the protons match with that of the expected structure. The ^1H NMR spectrum of **BTCD-PPV** is noisy because of its poor solubility, but the peaks are identical to **MTCD-PPV** (except the peak for $\text{Ar}-\text{OCH}_3$). One of the limitations normally noticed in the earlier reports based on bulky PPVs of adamantyl, cholastanyl, and cyclohexylmethylene was the poor characterization of the polymers by the NMR technique.^{24,27} The reason was mainly due to either the poor solubility of polymers for NMR characterization or the difficulty in the identification of protons corresponding to different subunits in the polymer backbone. Interestingly, in the present investigation, we could determine the composition of the TCD-based copolymers exactly from their ^1H NMR spectra. The peak corresponding to the $\text{Ar}-\text{OCH}_2$ protons in the 2-ethylhexyl unit (peak b) is merged with $\text{Ar}-\text{OCH}_3$ (peak a) in **MEH-PPV** (Figure 1a), whereas in **MTCD-PPV** (Figure 1d), $\text{Ar}-\text{OCH}_2$

protons (peak b') in the TCD unit appear separately from $\text{Ar}-\text{OCH}_3$ (peak a'). Therefore, the comparison of parts a and d of Figure 1 suggests that peaks a'' and b'' in the copolymers **P-4** and **P-6** correspond to $\text{Ar}-\text{OCH}_3 + \text{Ar}-\text{OCH}_2$ and $\text{Ar}-\text{OCH}_2$ in the MEH and BTCD aromatic rings, respectively. The intensities of a'' and b'' directly reflect the composition of the MEH and BTCD units in the copolymers, and the values determined by ^1H NMR are summarized in Table 1. The amount of BTCD in the feed vs incorporation in the copolymer is plotted and shown in Figure 2. The data fits in a straight line, which indicates that the copolymers follow a linear behavior irrespective of their monomer ratio in the feed. For **P-1** and **P-2**, peak b'' is completely merged with a'' and, therefore, it was not

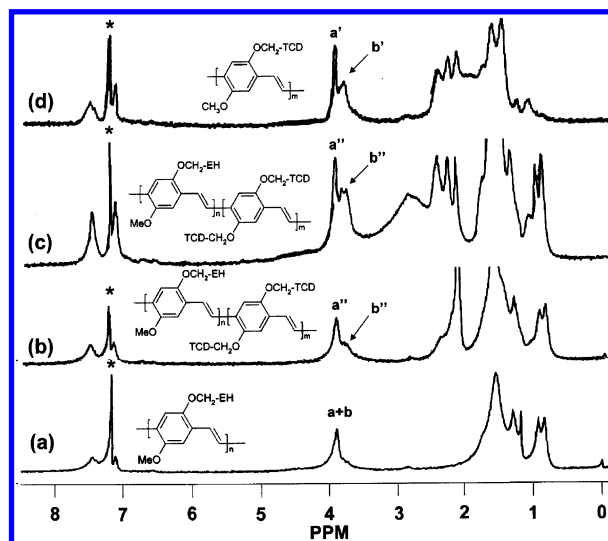


Figure 1. ^1H NMR spectra of **MEH-PPV** (a), **P-4** (b), **P-6** (c), and **MTCD-PPV** (d) in CDCl_3 . The peaks indicated by the asterisk are corresponding to CHCl_3 in CDCl_3 .

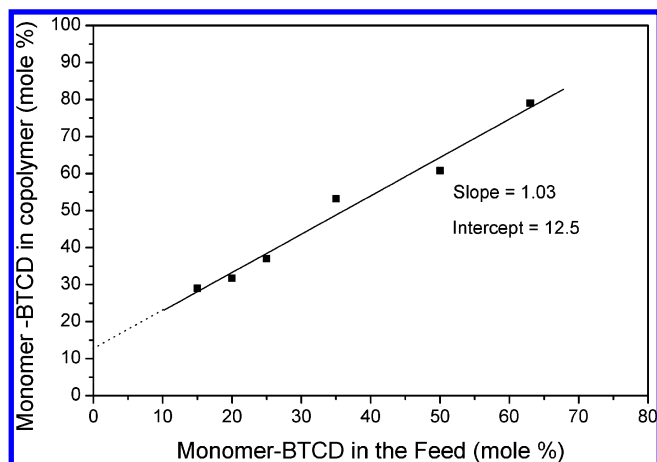


Figure 2. Plot of the amount of BTCD in the feed vs that in the copolymers.

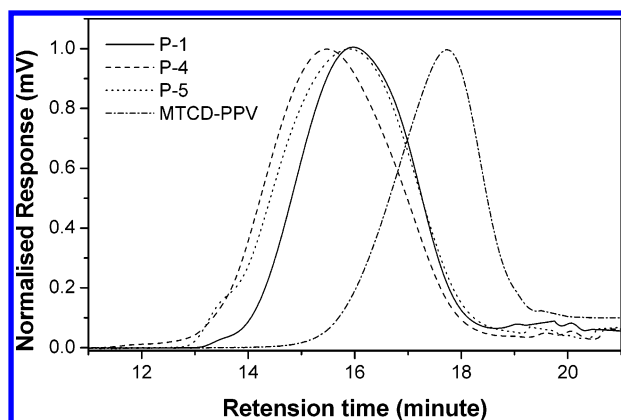


Figure 3. GPC plots of polymers.

possible to determine the actual composition of the copolymers. To determine the compositions in these two cases, the straight line plot was extra-plotted to obtain the values. The intercept of the straight line of 12.5 indicates that monomer **6** is highly reactive compared to **9** in the copolymerization reaction, which leads to the higher incorporation of TCD content in the copolymers irrespective of the feed ratio.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in THF using both RI and UV-vis detectors and polystyrene as standards for calibration. The number and weight average molecular weights (M_n and M_w), polydispersities, and number average degree of polymerization (n) of the polymers are summarized in Table 1. The GPC plot for the MTCD-PPV and copolymers **P-1**, **P-4**, and **P-5** is shown in Figure 3. MTCD-PPV and all the copolymers have a monomodal distribution, and no peak corresponding to the oligomer species is seen, which confirms the formation of high molecular weight polymers. In the present investigation, the molecular weight of MEH-PPV obtained was as high as $M_w = 161\,000$ (P. D. 3.4), which suggests that the experimental conditions adopted for the synthesis of PPVs were comparable to that of literature reports.^{9,40} Therefore, the differences in the molecular weights of the polymers are mostly related to the geometry of its monomers and not due to the polymerization conditions. In the case of MTCD-PPV and BTCD-PPV, the complete molecular weight of the polymers could not be determined by GPC, due to their partial solubility in THF. The degree of polymerization of THF soluble MTCD-PPV fractions indicates that it has more than 18 repeating units, which confirms that the molecular weight of the entire polymers

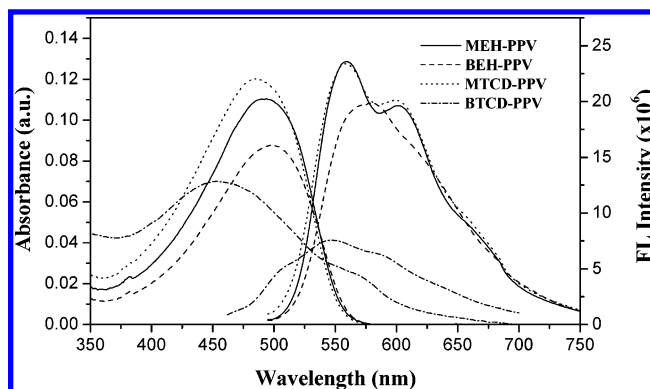


Figure 4. Absorbance and fluorescence spectra of homopolymers in CHCl_3 .

may be as high as MEH-PPV. It is very important to note that with increasing BTCD incorporation, the molecular weight of the copolymer showed a decreasing trend. For polymers having more than 50 mol % of the BTCD units (**P-6** and **P-7**), the molecular weights are approximately half of the other copolymers. This may be due to the fact that the bulky substituents induce steric hindrance at the polymerizable functional groups in the chain ends and make them not available for further growth. The number of repeating units (n) in **P-6** and **P-7** were determined to be 11 and 14, respectively. It is also important to mention that the solubility of copolymers tends to decrease and the polymer starts to precipitate out from the polymerization medium for higher BTCD incorporation (> 63%), which also restricts the formation of higher molecular weight polymers. Chou et al. also observed in their silsesquioxane PPVs that the molecular weight of PPVs decreases even for a 10 mol % increase in the amount of bulky substituted monomer in the feed.³² Therefore, in the BTCD-PPV copolymers, both steric hindrance and solubility play a major role in the formation of higher molecular weight polymers.

The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA), and all the polymers have a very good thermal stability up to 285–300 °C (see Table 1). The polymers showed the first degradation step at 280–290 °C and the second one at 350–375 °C (given in the Supporting Information). The degradation temperature for a 10 wt % loss is given in Table 1, and the values suggest that the bulky PPVs and their copolymers have high thermal stability similar to that of MEH-PPVs. Though **P-6** and **P-7** had low molecular weights, their high degradation temperature suggests that they are thermally stable for device fabrications and the obtained molecular weights are sufficient for further analysis. The thermal properties such as T_g , T_m , and T_c of the polymers were investigated by differential scanning calorimetry (DSC). All the polymers were found to be amorphous, and no melting or crystallization peaks appeared in the heating/cooling cycles. The glass transition is very weak for MTCD-PPV and difficult to determine, but the BTCD-PPV showed a weak glass transition at 115 °C, which is 40–50 °C higher than that of MEH-PPV. It indicates that the TCD substitution in PPV increases the rigidity of the polymer chain and thereby increases T_g .

The absorbance and photoluminescence (PL) spectra of the polymers were recorded in chloroform and in films on a glass plate and shown in Figures 4 and 5. The solution absorbance spectrum of MTCD-PPV is almost identical to that of MEH-PPV, whereas the BTCD-PPV is blue shifted by 28 nm followed by an increase in steric hindrance. The emission spectra of the polymers were recorded using λ_{max} (abs) as the excitation wavelength. The solution emission spectra for all the polymers

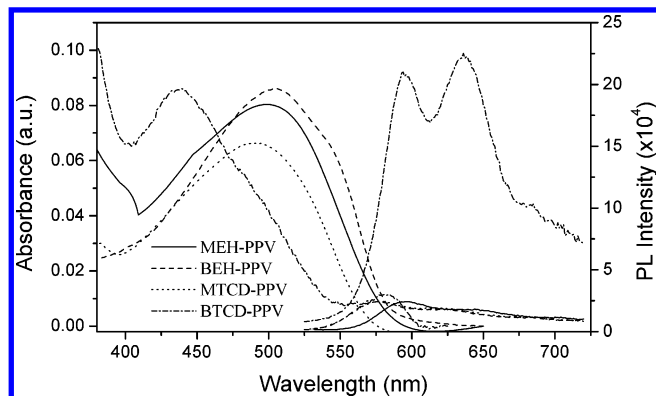


Figure 5. Absorbance and fluorescence spectra of homopolymers in film.

are almost identical except a small difference in the luminescence maxima. This suggests that the influence of a bulky TCD unit is very weak in solution and the properties are almost identical to that of **MEH-PPV**. In the solid state (film, Figure 5), the absorbance spectrum of **MTCD-PPV** is slightly blue shifted compared to that of **MEH-PPV**, but the **BTCD-PPV** showed a large blue shift of 50 nm indicating that the steric hindrance caused by the bulky group is very significant in the solid state compared to that in solution. Interestingly, the intensity of the PL spectrum of **BTCD-PPV** is enhanced more than 4–5 times compared to that of **MTCD-PPV**, **MEH-PPV**, and **BEH-PPV**. The emission maxima of all the polymers varied within 10–15 nm only, suggesting that though they significantly differed in the intensity of their luminescence, the emission color remained almost unchanged. The introduction of bis-TCD units in the backbone enhances the luminescence intensity of PPV in the solid state without affecting the color of the emission. The comparison of the solid-state absorbance and emission spectra also reveals that although there is a large difference in the absorbance maxima between **BTCD-PPV** and other polymers (50 nm), in the excited state they all form similar emissive species, which is evident from their PL spectra. Therefore, the increase in the PL intensity in **BTCD-PPV** is not due to the difference in the emissive species in the excited state and may be related to their difference in the quenching process. The PL experiments were repeated at different positions in the same film and also for at least two different samples over a period of 30 days. The results were identical, which confirmed that the large enhancement in the PL intensity arose from the difference in the structure and not due to any experimental error.

The space-filling model of the **BTCD-PPV** and **MTCD-PPV** polymer segments (shown in the Supporting Information) suggests that the **MTCD-PPV** segments have more free space because of the preferred random orientation of the TCD unit on either side of the backbone. On the other hand, in the **BTCD-PPV**, the symmetrically substituted TCD unit prevents interdigitization of the polymer chains, thus increasing the interchain distance, which in turn controls the formation of microaggregates in PPV and enhances the PL intensity. In the case of **MTCD-PPV**, polymer chains are relatively closely packed as in the case of **MEH-PPV**, and therefore, the emission properties are almost identical to that of the latter. However, the space-filling model can only describe the aggregation process in 2D, but the vertical packing (3D) of polymer chains may also influence the PL intensity. To analyze the vertical packing of the polymer chains, the emission spectra of the polymers were recorded for films of various thickness. The polymer concentration and speed of the film casting unit was controlled manually to produce samples of various film thicknesses for the photoluminescence

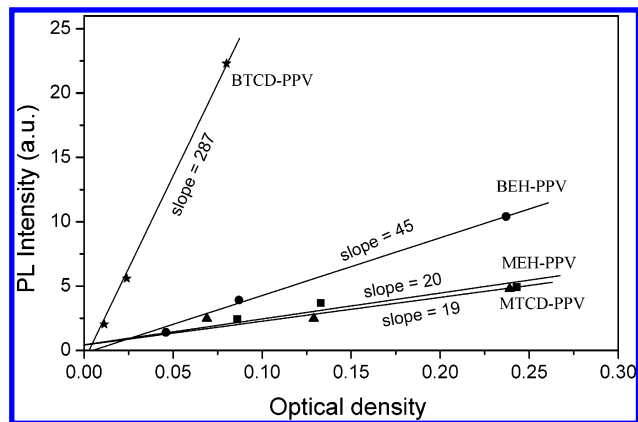


Figure 6. Plot of optical density vs the photoluminescence intensity in film.

studies. Since the optical density (OD) of the film (λ_{max} (abs)) is directly proportional to the film thickness, the influence of 3D molecular aggregation on luminescence properties can be analyzed by plotting the PL intensities with respect to their ODs. The PL intensities of the various films were plotted against their ODs and shown in Figure 6 indicating its linear increase with the OD. The slope of the plots were obtained by line fitting ($Y = mX + C$) as 287, 45, 20, and 19 for **BTCD-PPV**, **BEH-PPV**, **MEH-PPV**, and **MTCD-PPV**, respectively. The linearity of the curves for all the polymers indicates that the increase in the intensity of the emission is common to the entire bulk three-dimensionally and not restricted to isolated domains or layers in the polymer films. Therefore, the difference in the slope of the curves can be directly correlated to the difference in the luminescence efficiency of the polymers. The slope of **MTCD-PPV** is almost identical to that of **MEH-PPV**, suggesting that the bulkiness afforded by mono-TCD substitution in PPV is not enough to result in a significant enhancement of luminescence intensity. On the other hand, the bis-TCD substitution enhances the luminescence intensity significantly and the enhancement is more than 6 times higher compared to that of BEH and 15 times higher than that of EH substitution in PPV. It clearly demonstrates that the bis-TCD unit is very rigid and capable of increasing the interchain distances in PPV, thus controlling the molecular aggregation, leading to significant enhancement in the solid-state photoluminescence.

To study the composition of bulky substituents on the photophysical properties of **MEH-PPV** chains, the copolymers **P-1–P-7** were prepared using the BTCD monomer along with the **MEH-PPV** monomer as described in Scheme 2. The copolymers containing mono-TCD substituents in **MEH-PPV** were not studied further because the OD vs PL intensity plots (Figure 6) for its parent polymers **MEH-PPV** and **MTCD-PPV** are almost identical. Therefore, the incorporation of the mono-TCD unit in the **MEH-PPV** backbone may not contribute significantly to the luminescence properties of the latter. The luminescence plots for the copolymers in solution and film are shown in Figures 7 and 8, respectively. The absorption and emission data for the copolymers are summarized along with those of the homopolymers in Table 2. The emission spectra of the copolymers in solution (Figure 7) indicate that the features are almost identical to that of **MEH-PPV**. Interestingly, the solid-state spectra are different from their solution, and the emission spectra of the copolymers indicate that the luminescence intensity increases with an increasing amount of BTCD content in the **MEH-PPV**. The copolymers having more than 50% of BTCD units (**P-5–P-7**) showed a large increase in their luminescence intensities, which are equal to that of its homopoly-

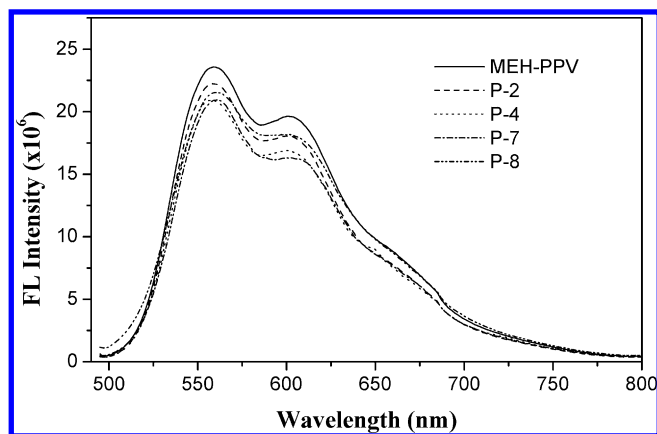


Figure 7. Fluorescence spectra of MEH-PPV and copolymers in CHCl_3 .

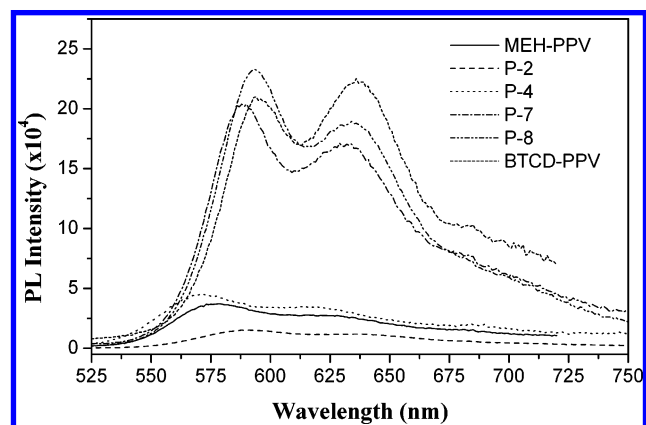


Figure 8. Photoluminescence spectra of MEH-PPV, BTCD-PPV, and copolymers in film.

mer, **BTCD-PPV** (see Table 2). The present investigation reveals that the incorporation of 50 mol % of BTCD is sufficient enough to attain the maximum luminescence intensity possible in **MEH-PPV**. The quantum yields of the homo- and copolymers were also determined using Rhodamine 6G as a standard and summarized in Table 2. The quantum yield values are plotted against the BTCD incorporation in **MEH-PPV** and shown in Figure 9. The quantum yield for **MEH-PPV** is obtained as 0.16, which is in the range reported by earlier reports.⁹ The quantum yield of **MTCD-PPV** is almost double compared to that of MEH and **BEH-PPV**. This indicates that **MTCD-PPV** is very attractive for application in optoelectronics. Interestingly, the quantum yield of the copolymers increases

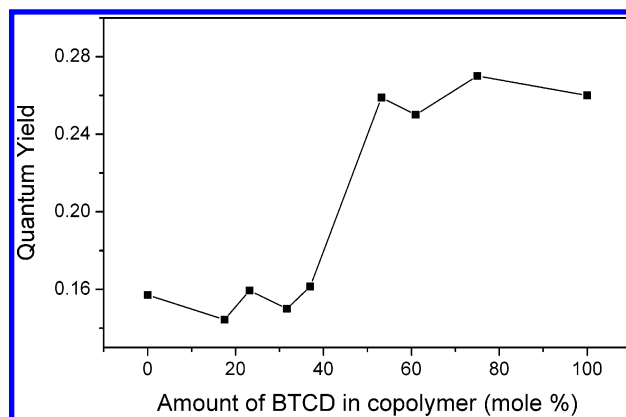


Figure 9. Plot of quantum yield vs the amount of BTCD in the copolymer.

with the increase in the BTCD content and attained a plateau for samples with >50 mol % incorporation (Figure 9). This is almost similar to the behavior observed for the PL intensity increase in the film for the copolymers (Figure 8). The combination of Figures 8 and 9 indicates that the presence of more than 50% of BTCD in **MEH-PPV** increases the quantum yield twice in solution as well as 4–5 times in PL intensity.

Conclusion

New tricyclodecane-substituted PPVs were synthesized through a halo-precursor route, and the present approach demonstrates that the π -stacking-induced aggregates can be controlled, resulting in a large enhancement of solid-state photoluminescence. Two new PPVs were synthesized from a commercially important and economically cheap TCD unit, which may be very attractive for applications in highly luminescent polymer LEDs. A new series of highly soluble bulky PPV copolymers were also prepared, and their photophysical properties reveal that only 50 mol % of symmetrical TCD units is needed for producing maximum luminescence efficiency from the **MEH-PPV** chains. The new bulky PPV copolymers are highly soluble, thermally stable, highly luminescent, and economically cheap compared to materials reported so far for the bulky approach in the π -conjugated systems. Additionally, the intermediate molecules **3** and **4** reported here are very attractive for synthesizing various other highly luminescent bulky π -conjugated polymers such as poly(*p*-phenylene)s and poly(*p*-phenylenethynylene)s based on TCD. We are currently exploring various bulky conducting polymers based on this approach for applications in optoelectronics.

TABLE 2: Absorption and Emission Properties of the Polymers

polymer	λ_{max} (abs) in CHCl_3 (nm)	λ_{max} (em) ^a in CHCl_3 (nm)	ϕ_{em} ^b	λ_{max} (abs) in film (nm)	λ_{max} (em) ^c in film (nm)	PL intensity (counts $\times 10^4$)
MEH-PPV	497	561	0.16	503	592	3.7 (0.13) ^d
BEH-PPV	501	582	0.19	505	578	4.0 (0.09)
MTCD-PPV	495	561	0.29	495	580	2.5 (0.13)
P-1	492	558	0.14	497	591	1.5 (0.13)
P-2	499	560	0.16	504	584	3.2 (0.12)
P-3	488	559	0.15	503	571	5.3 (0.14)
P-4	495	559	0.16	501	573	4.5 (0.26)
P-5	483	567	0.26	485	570	14.0 (0.12)
P-6	493	561	0.25	509	589	20.3 (0.14)
P-7	491	561	0.27	496	593	23.2 (0.11)
BTCD-PPV	430	581	0.26	426	588	22.5 (0.08)

^a Excitation wavelength is 480 nm for all the polymers. ^b Calculated using Rhodamine 6G as the standard and 480 nm as the excitation energy; the absorbance of the solution is maintained as 0.1. ^c Excitation wavelength is the absorbance maximum. ^d The values in the bracket correspond to absorbance at the maximum.

Acknowledgment. This work was funded by KSCSTE-Thiruvananthapuram, Kerala, India. We greatly acknowledge Celanese Chemicals Ltd. for providing TCD research samples. We also thank Dr. Suresh Das, RRL-Trivandrum, for the luminescence measurements.

Supporting Information Available: Space-filling model for the bulky PPVs and TGA plots are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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