

# Synthesis of Novel Conjugated Polymer Based on Cyclopenta[def]phenanthrene and Vinylene with Strong Interchain Interaction

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**ABSTRACT:** In this study, a novel conjugated polymer, poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[def]phenanthrene-2,6-vinylene) (PCPPV) has been synthesized and characterized. For the polymerization, Gilch's reaction was applied for the first time with the cyclopenta[def]phenanthrene system. The absorption and emission spectra of PCPPV are red-shifted about 40–50 nm due to the vinylene units when compared with those of poly(2,6-(4,4-bis(2-ethylhex-yl)-4*H*-cyclopenta[def]phenanthrene)) (PCPP). The solid-state fluorescence is significantly broadened, possibly due to  $\pi$ – $\pi$  interactions introduced by the phenanthrene and vinylene moieties. In solution, as the concentration of polar solvent increased, the photoluminescence (PL) intensity decreased due to quenching and aggregation by the interchain interactions between the conjugated backbones. After annealing the film at 80 °C, the PL and electroluminescence (EL) emission spectra exhibited also the quenching and aggregation effects indicating the interchain interactions of PCPPV. The large number of aromatic rings in a unit and the increased planarity achieved through introduction of vinylene units are able to give interchain interactions stronger than fluorene or phenylene units. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 5068–5077, 2009

**Keywords:** conjugated polymers; fluorescence; Gilch reaction; interchain interaction; PCPPV; synthesis

## INTRODUCTION

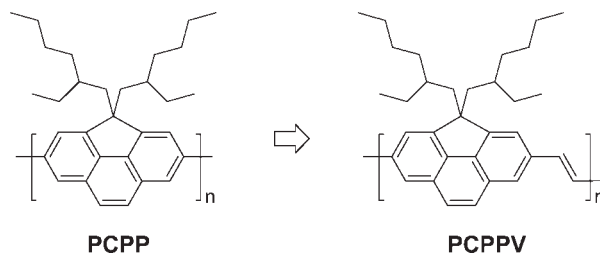
Various kinds of conjugated polymers such as poly(phenylenevinylene) (PPV),<sup>1</sup> poly(*p*-phenylene) (PPP),<sup>2</sup> poly(thiophene),<sup>3</sup> poly(fluorene) (PF),<sup>4</sup> along with their copolymers, and soluble

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derivatives have been investigated comprehensively for the research in the field of electroluminescent materials.<sup>5–9</sup> Such polymers possess remarkable electronic and optical properties as a consequence of electron delocalization within their  $\pi$ -orbitals, making their prospective application as large-area light emitting diodes (LEDs)<sup>10–13</sup> and polymer photovoltaic cells.<sup>14–18</sup> Low band gap polymers are necessary as electron donor in polymer solar cells. Conjugated polymers with low band gaps are especially creating much interest as they can be used as a host for red electrophosphorescent dopants with their blends and copolymers capable of emitting adjustable red light by energy transfer.<sup>19–23</sup> Since these low band gap polymers are covering wide range of visible spectra, they can be used for the purpose of improving the efficiency of the solar cell. Although aggregation effect by the intermolecular interaction of the polymer backbone has been a disadvantage in PLEDs system, it could be advantageous for the polymer solar cell system because of their broad absorption spectra in visible range. Besides, when these types of polymers are used as the polymer donor in solar cell, it could be able to increase the intermolecular interaction between polymer donor and acceptor, which is favorable for the electron transfer.

It is well known that polyfluorenes (PFs) are very attractive blue emitting materials due to the remote C-9 position that provides the desirable solubility for processability of polymers, all without appreciably increasing the steric interactions in the polymer backbone.<sup>24,25</sup> The PFs show high photoluminescence (PL) efficiency and good charge transport. However, PFs do have a tendency to generate long wavelength emissions around 550 nm, either during annealing or passage of current, turning the desired blue emission color into an undesired blue–green emission, along with a drop in electroluminescence (EL) quantum efficiency.<sup>26–28</sup> PF derivatives, which have been synthesized as new materials with high carrier mobilities and absorption spectra to match the solar spectrum, have also been introduced in polymer solar cells to increase the photocurrent as much as possible.<sup>29</sup> Because of the low charge mobility in most conjugated polymers, the interchain interactions within active layers can be an important factor to increase the power-conversion efficiency of a solar cell. The bulk heterojunction solar cells fabricated using blends of polymers with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) can exhibit varied perform-



**Figure 1.** Polymer structure of PCPPV with cyclopenta[def]phenanthrene units.

ances,<sup>30,31</sup> depending on the interchain interactions between polymer and PCBM.

In our previous contribution, synthesis and properties of a polymer utilizing a new poly(2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene)) (PCPP) backbone, with stabilized pure blue emission, have been reported.<sup>32–34</sup> PL and EL spectra of PCPP did not show any peaks in the long wavelength region corresponding to keto defect sites or aggregates/excimers, even after annealing the device for 18 h in air or operation of the device for 40 min. Moreover, the properties of many poly(fluorene-vinylene) and poly(phenanthrylene-vinylene) derivatives have also been reported.<sup>35–38</sup> Therefore, efforts should be made to incorporate the research of polymer backbones with phenanthrene and vinylene units to exploit new conjugated backbones as polymer solar cells. Herein, we report the synthesis and characterization of a new conjugated polymer with a phenanthrene backbone, poly(4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene-2,6-vinylene) (PCPPV). To induce the intermolecular interaction, a vinylene group was incorporated into the phenanthrene backbone. PCPPV was synthesized via the Gilch's reaction, which modified the recently reported method (Fig. 1).

## EXPERIMENTAL

### Materials and Instruments

All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian-Gemini-300 (300 MHz) spectrometer, and chemical shifts were recorded in ppm units with TMS as the internal standard. Cyclic voltammetric wave was produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan

rate of 100 mV/s. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The PL and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, xenon lamp was used as the excitation source, and incident beam took the maximum absorption peak of the polymers. Molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration by using THF solution. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between the emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spin coated on the surface-treated ITO substrate. On top of the PEDOT/PSS layer, the emissive polymer film was obtained by spin casting *o*-dichlorobenzene (ODCB) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and aluminum electrodes were deposited on top of the polymer films through a mask by vacuum evaporation at pressures below  $10^{-7}$  Torr, yielding active areas of 4 mm<sup>2</sup>. For the determination of device characteristics, current-voltage (*I*-*V*) characteristics were measured using a Keithley 236 source measure unit. All the aforementioned processing steps and measurements were carried out under air and at room temperature. To examine the electrochemical properties of the resulting polymer, the polymer film was cast from THF solution onto a platinum plate as a working electrode.

### Synthesis of Monomer and Polymer

#### **4,4-Bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene-2,6-dicarbaldehyde (6)**

To a stirred solution of 4.60 g (8.04 mmol) of 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene (**5**) in 30 mL of dry tetrahydrofuran at  $-78^{\circ}\text{C}$  under Ar condition, 12.60 mL (20.09 mmol) of *n*-BuLi (1.6 M in hexane solution) was added. After 40 min at  $-78^{\circ}\text{C}$ , 6.16 mL (80.35 mmol) of 4-formylmorpholine was added for 20 min, and the reaction was kept at room temperature and stirred for 2 h. The reaction mixture was quenched with brine and extracted into methylene chloride. The organic phase was

dried with  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography (40  $\times$  200 mm column,  $\text{SiO}_2$ , ethyl acetate:hexane = 1:20) to give 2.79 g (65%) of extremely clean compound **6**, pale yellow solid; mp:  $77^{\circ}\text{C}$ ,  $R_f$ : 0.35 ( $\text{SiO}_2$ , ethyl acetate:hexane = 1:20).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.30 (s, 2H), 8.38 (s, 2H), 8.16 (t,  $J = 3.3$  Hz, 2H), 8.03 (s, 2H), 2.26 (m, 4H), 0.44–0.81 (m, 30H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 193.03, 151.81, 140.93, 137.44, 129.63, 128.72, 127.18, 119.74, 59.52, 44.10, 35.54, 34.08, 28.24, 27.45, 22.73, 14.03, 10.44; HRMS ( $m/z$ , FAB): Calcd for  $\text{C}_{33}\text{H}_{42}\text{O}_2$  470.3185, Found 470.3187.

#### **[4,4-Bis(2-ethylhexyl)-6-(hydroxymethyl)-4H-cyclopenta[def]phenanthrene]-methanol (7)**

To a stirred solution of 1.21 g (2.57 mmol) of 4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene-2,6-dicarbaldehyde (**6**) in 50 mL of dried methylene chloride at  $-78^{\circ}\text{C}$  under nitrogen, 7.70 mL (7.70 mmol) of diisobutylaluminum hydride (1.0 M in THF solution) was added. After 2 h at  $-78^{\circ}\text{C}$ , the reaction mixture was cautiously treated with 1 mL of methanol, warmed to room temperature, and diluted with 50 mL of ether. This solution was washed with 10 mL of a saturated aqueous sodium tartrate solution. The total aqueous extracts were washed with 2  $\times$  50 mL of ether, and the combined organic extract was dried ( $\text{MgSO}_4$ ) and concentrated. The oily residue was purified by flash chromatography (40  $\times$  200 mm column,  $\text{SiO}_2$ , ethyl acetate:hexane = 1:4) to give 1.02 g (84%) of diol compound **7**, a yellow oil:  $R_f$ : 0.35 ( $\text{SiO}_2$ , ethyl acetate:hexane = 1:3).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.57 (s, 2H), 7.76 (s, 2H), 7.79 (s, 2H), 4.95 (s, 4H), 2.17 (m, 4H), 0.45–0.88 (m, 30H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 150.15, 140.42, 137.17, 127.65, 125.75, 121.59, 120.32, 66.99, 59.15, 44.14, 35.38, 34.20, 28.37, 27.45, 22.88, 14.15, 10.48; HRMS ( $m/z$ , FAB): Calcd for  $\text{C}_{33}\text{H}_{46}\text{O}_2$  474.3498, Found 474.3501.

#### **2,6-Bis(chloromethyl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene (8)**

To a stirred solution of 1.65 mL (3.30 mmol) of oxalylchloride in 20 mL methylenechloride at  $0^{\circ}\text{C}$  under nitrogen, 0.23 mL of *N,N*-dimethylformamide was slowly added over 3 min. The resulting white suspension was kept at room

temperature for about 10 min, recooled again at 0 °C, and added 0.63 g (1.32 mmol) of [4,4-bis(2-ethylhexyl)-6-(hydroxymethyl)-4*H*-cyclopenta[*def*]phenanthrene]-methanol (**7**). The reaction mixture was stirred at 0 °C for 1 h poured into 100 mL saturated aqueous sodium chloride, and extracted with 2 × 20 mL of ether. The organic phase was dried with MgSO<sub>4</sub> and concentrated under reduced pressure. Flash chromatography (40 × 100 mm column, SiO<sub>2</sub>, hexane) to give 0.60 g (90%) of dichloride compound **8**, a yellow solid; mp: 67 °C, *R*<sub>f</sub>: 0.34 (SiO<sub>2</sub>, hexane 100%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.82 (s, 2H), 7.79 (s, 2H), 7.61 (s, 2H), 4.89 (s, 4H), 2.19 (m, 4H), 0.48–0.86 (m, 30H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 150.41, 137.26, 137.07, 127.69, 125.92, 123.54, 121.81, 59.37, 48.19, 44.06, 35.41, 34.44, 28.49, 27.53, 22.84, 14.13, 10.48; HRMS (*m/z*, FAB) Calcd for C<sub>33</sub>H<sub>44</sub>Cl<sub>2</sub> 510.2820, Found 510.2822.

#### Poly(p-cyclopenta[*def*]phenanthrenevinylene)

To a stirred solution of 0.59 g (1.15 mmol) of 2,6-bis(chloromethyl)-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene (**8**) in 20 mL of THF at 40 °C under nitrogen, 6.92 mL (6.92 mmol) of 1.0 M solution of potassium *tert*-butoxide in THF was added by a syringe pump over 1 h. Upon addition, the reaction mixture had color change from colorless via greenish to yellow, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred for 10 h at room temperature, and 0.42 mL of 4-*tert*-butylbenzylbromide was added to form an end-capping. The reaction mixture was slowly poured into 200 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with methanol, and dried under reduced pressure at room temperature to generate the crude polymer as yellow powder. The resulting polymer was redissolved in 200 mL of chloroform at 80 °C, cooled to 40 °C, and reprecipitated by dropwise addition of 500 mL of methanol. The precipitated polymer was filtered and dried at room temperature under reduced pressure to generate PCPPV. 167 mg (28%) of PCPPV was obtained as a light yellow polymer (Fig. 2).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.60–8.09 (m, 6H), 2.22 (br, 4H), 0.58–1.68 (br, 30H); FTIR (film, cm<sup>-1</sup>): 2924, 2855, 1740, 1459, 1375, 1249, 1167.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

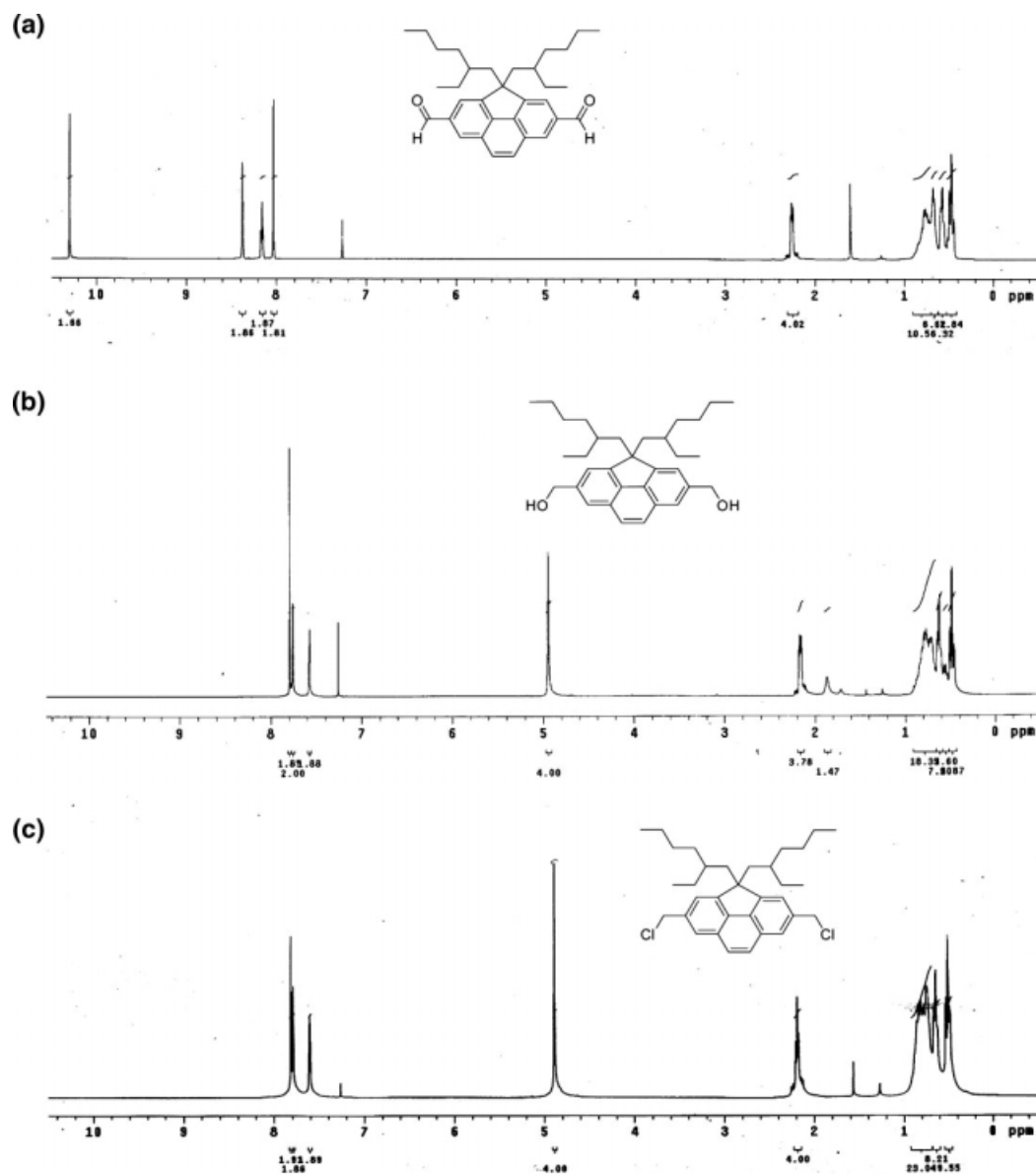
The general synthetic route toward the monomer and polymer is outlined in Scheme 1 and begins with the hydrogenation of 4*H*-cyclopenta[*def*]phenanthrene (**1**) with Pd/C to generate 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**). Alumina-supported copper(II) bromide provided 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**3**) with high selectivity. Compound **3** was then dehydrogenated using Br<sub>2</sub> and CS<sub>2</sub> to afford 2,6-dibromo-4*H*-cyclopenta[*def*]phenanthrene (**4**), which was converted to 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene (**5**), using 2-ethylhexyl bromide, 50% aqueous NaOH, and catalytic amounts of triethylbenzylammonium chloride.<sup>34</sup> The formylation of **5** using *n*-butyllithium in hexane and 4-formylmorpholine in THF to give 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene-2,6-dicarbaldehyde (**6**), which was then converted to diol **7** by DIBAL reduction, which upon chlorination with oxalyl chloride in DMF and dichloromethane generated chloromethyl cyclopenta[*def*]phenanthrene (**8**). This monomer was used for the preparation of PCPPV by Gilch's polymerization, employing an excess amount of potassium *tert*-butoxide in THF at 0 °C for 24 h under Ar atmosphere.

The resulting polymer was soluble in organic solvents such as chloroform, tetrahydrofuran, dichloromethane, and chlorobenzene. The number-average molecular weight (*M*<sub>n</sub>) and the weight-average molecular weight (*M*<sub>w</sub>) of polymers were 70,000 and 187,000 with a polydispersity index (*M*<sub>w</sub>/*M*<sub>n</sub>) of 2.6 as determined by GPC using THF as the eluant and polystyrene as the standard. Its high thermal stability was determined through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in nitrogen (Table 1). DSC was performed in the temperature range from 30 to 430 °C to show that the glass transition temperature (*T*<sub>g</sub>) of 76 °C. The decomposition temperature (*T*<sub>d</sub>), which correspond to a 5% weight loss upon heating during TGA, was around 380 °C.

### Absorption and Photoluminescence Properties of Polymer

The optical absorption and photoluminescence (PL) properties of PCPPV were investigated both in THF solutions and thin solid films. The



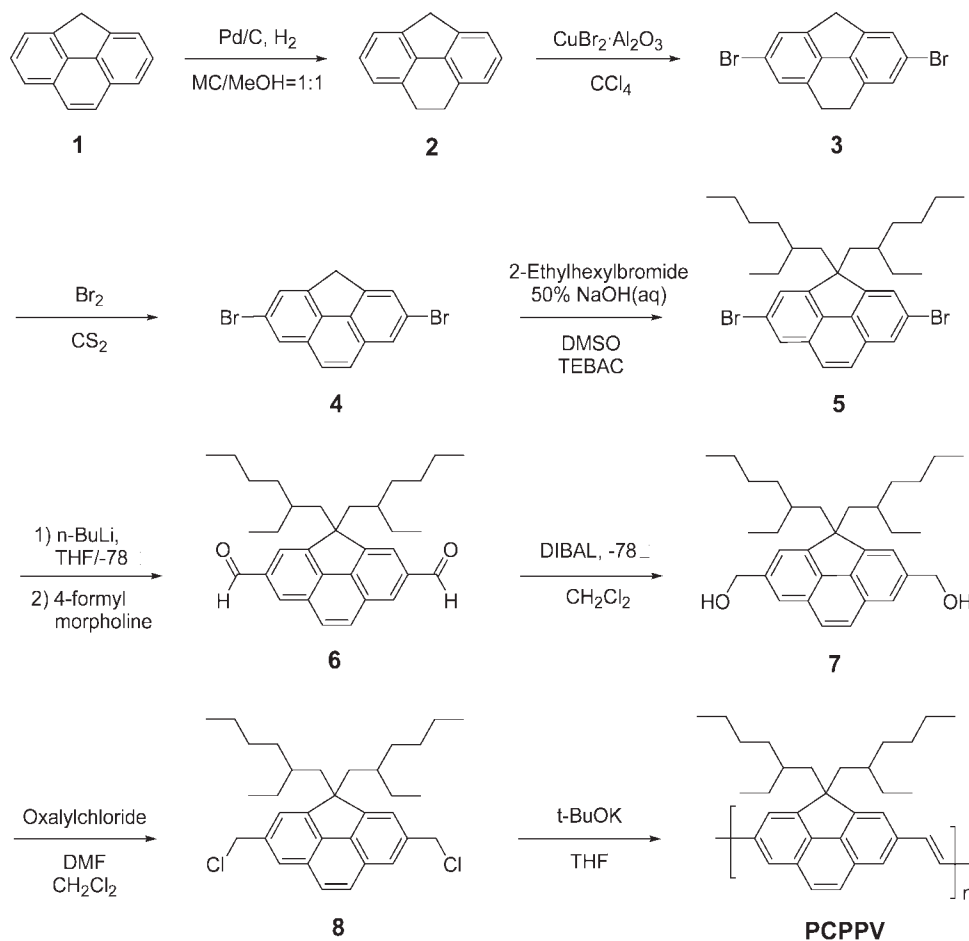


**Figure 2.**  $^1\text{H}$  NMR of Compound **6** (a), **7** (b), and **8** (c).

concentrations of all the THF solutions were fixed at  $1 \times 10^{-5}$  M. Transparent and uniform polymer films were prepared on quartz plates by spin casting from their respective ODCB solution at room temperature. The absorption and emission data for PCPPV are summarized in Table 2. There is less difference between the absorption and emission spectra of PCPPV in the solutions and the thin films, which can be attributed to the  $\pi$ - $\pi^*$  transitions of the polymer.

The optical properties of PCPPV in THF and as a thin film are shown in Figure 3. The absorption and emission spectra of PCPPV are red-shifted

about 40–50 nm due to the vinylene units, when compared with that of PCPP, whereas the rigid biphenyl unit within cyclopentaphenanthrene reduced the emission wavelength of the polymer. The absorption spectra in THF and as a thin film are similar with PCPPV exhibiting a maximum absorption peak at 400 nm. The fluorescence spectrum of PCPPV showed an emission at 450 nm in solution, considerably red-shifted from the PL spectrum of PCPP (ca. 410 nm). The solid-state fluorescence is only slightly red-shifted from the polymer in solution, but is significantly broadened, possibly due to additional  $\pi$ - $\pi$  interactions



**Scheme 1.** Synthetic route for the monomer and the polymer (PCPPV).

or conformational rigidity in the solid state as a consequence of the rigid biphenyl linkage introduced by the phenanthrene moieties.<sup>20</sup>

### Electrochemical Properties of the Polymer

The electrochemical properties of the polymers were determined from the band gaps estimated from the absorption edges and the highest occupied molecular orbital (HOMO) energy levels, which were estimated from cyclic voltam-

metry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ , 0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of argon. A platinum electrode ( $\sim 0.05 \text{ cm}^2$ ) coated with a thin polymer film was used as the working electrode. Pt wire and an Ag/AgNO<sub>3</sub> electrode were used as the counter and reference electrodes, respectively. The energy level of the Ag/AgNO<sub>3</sub> reference electrode (calibrated by the FC/FC<sup>+</sup> redox system) was 4.8 eV below the vacuum

**Table 1.** Results of Polymerization

Polymer	$M_n^a (\times 10^3)$	$M_w^a (\times 10^3)$	PDI <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$T_d$ (°C) <sup>c</sup>
PCPPV	70	187	2.60	76	380

<sup>a</sup> Molecular weight ( $M_w$ ) and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards.

<sup>b</sup> Glass transition temperature measured by DSC under N<sub>2</sub>.

<sup>c</sup> Onset decomposition temperature (5% weight loss) measured by TGA under N<sub>2</sub>.

**Table 2.** Optical Properties of Polymer

Polymer	In Solution (nm)			In Film (nm)		
	Abs $\lambda_{\text{max}}$	PL $\lambda_{\text{max}}$	fwhm <sup>a</sup>	Abs $\lambda_{\text{max}}$	PL $\lambda_{\text{max}}$	fwhm <sup>a</sup>
PCPPV	403	449	42	398	453	62

<sup>a</sup> Full width at half-maximum of the PL spectra.

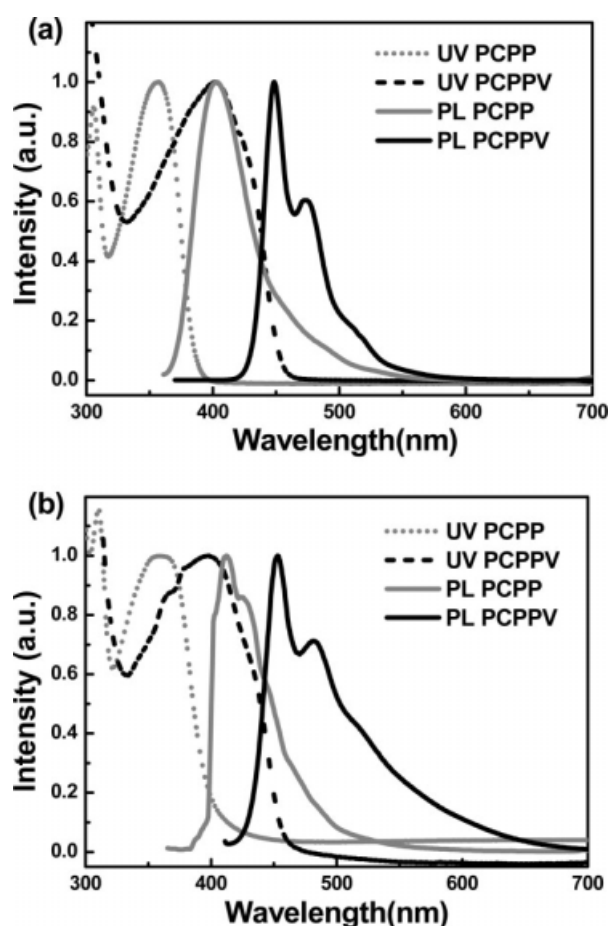
level. HOMO levels were calculated according to the empirical formula ( $E_{\text{HOMO}} = -[E_{\text{onset}}]^{\text{ox}} + 4.8$  eV). The oxidation potentials derived from the onset of electrochemical *p*-doping are summarized in Table 3. During the anodic scan, the oxidation onset potential of PCPPV was 0.80 V and exhibited irreversible *p*-doping process. HOMO energy level of the present polymer was −5.60 eV. The

absorption onset wavelength of PCPPV was observed to be 460 nm in the solid thin film, corresponding to the band gap of 2.70 eV. The lowest unoccupied molecular orbital (LUMO) energy level was calculated from the values of the band gap and HOMO energy level, and the value was −2.90 eV.

### Aggregation Effects of the Polymer

It is worthwhile to compare the PL spectra of PCPPV in varying mixtures of ODCB and MeOH (Fig. 4). In ODCB, the PL spectra of PCPPV showed the maximum peaks at 450 and 478 nm. As the concentration of MeOH increased, the PL spectra decreased since quenching and aggregation by the interchain interactions between the conjugated backbone could be induced in a polar solvent. In 50% MeOH, the PL spectra showed red-shifted maximum peaks from 450 and 478 nm to 457 and 487 nm, and the height ratio of the peak at 487 nm was increased, indicating that the quenching and aggregation in a polar solvent could be increased due to the enhanced  $\pi$ – $\pi$  interchain interactions of PCPPV by the planarity and rigidity of the materials.

A preliminary investigation of the physical properties of the polymer was carried out by means of PL and EL (Fig. 5). After annealing the film at 80 °C for 0, 5, 10, 20, 30, 40, 50, and 60



**Figure 3.** UV–vis absorption and photoluminescence emission spectra of PCPP and PCPPV in THF solution at a concentration of  $1 \times 10^{-5}$  mol/L (a) and solid thin film (b).

**Table 3.** Electrochemical Potential and Energy Levels of Polymer

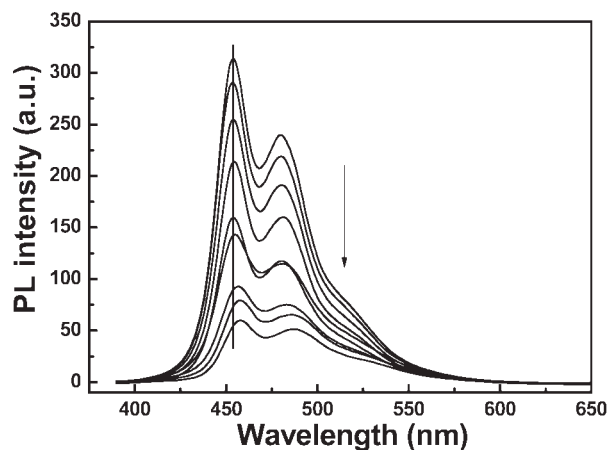
Polymer	$E_{\text{onset}}^{\text{a}}$ (V)	HOMO <sup>b</sup> (eV)	LUMO <sup>c</sup> (eV)	$E_{\text{g}}^{\text{d}}$ (eV)
PCPPV	0.80	−5.60	−2.90	2.70

<sup>a</sup> Onset oxidation potential measured by cyclic voltammetry.

<sup>b</sup> Calculated from the oxidation potential.

<sup>c</sup> Calculated from the HOMO energy levels and  $E_{\text{g}}$ .

<sup>d</sup> Energy band gap was estimated from the onset wavelength of the optical absorption.



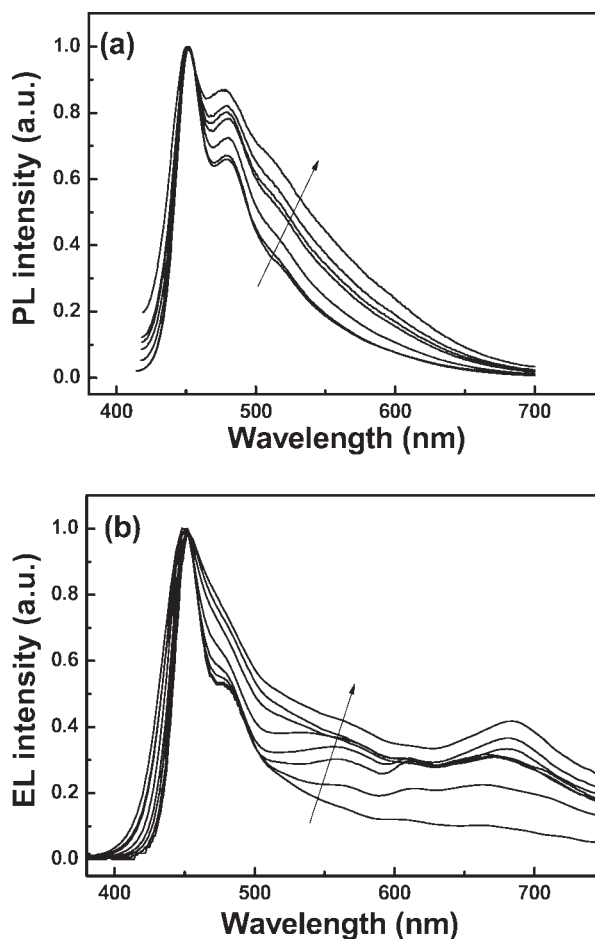
**Figure 4.** PL spectra of PCPPV ( $[PCPPV] = 1 \times 10^{-6}$  M) in the mixture solution of ODCB and MeOH (MeOH = 0–80%). All emission scans were collected by exciting at 380 nm.

min, the full-width at half-maximum (fwhm) and shoulder peaks of PL spectra were increased. Consequently, the emission features of PCPPV showed evidence of broadening of emission bands in the solid state because of the beneficial effect of the phenanthrene moieties and vinylene units deriving from strong intermolecular interactions.

Figure 5(b) shows the EL spectra of the device with the configuration of ITO/PEDOT/PCPPV/Al. The EL spectra of PCPPV exhibited a maximum peak at 450 nm, nearly identical with the PL spectrum. The emission color of the PCPPV device with the configuration of ITO/PEDOT/PCPPV/Al was blue with CIE coordinates of  $x = 0.22$  and  $y = 0.22$  at 5 V (Table 4). At increasing operating voltage, the emission color was changed from blue to white because of the broadening of the emission band, induced by the aggregation of the phenanthrene moieties and vinylene units due to intermolecular interactions. Herein, we conclude that the interchain interaction of PCPPV, which gives effect to the  $\pi$ – $\pi^*$  transitions of the conjugated backbone, could be due to the aggregation caused by the planarity of the materials in the solid state.

## CONCLUSIONS

In this study, a novel conjugated polymer PCPPV with CPP and vinylene units has been synthesized and characterized. For the polymerization, Gilch's reaction was applied for the first time with the cyclopenta[def]phenanthrene system. The



**Figure 5.** (a) PL spectra of PCPPV after annealing the film at 80 °C for 0, 5, 10, 20, 30, 40, 50, and 60 min. The excitation wavelength was 400 nm. Spectra are normalized to show increased fwhm. (b) EL spectra of OLEDs with configurations of the ITO (150 nm)/PEDOT (10 nm)/PCPPV (30 nm)/Al (150 nm) device at the different operating voltage (voltage = 5–12 V).

**Table 4.** CIE Coordinates with the Bias Voltage

Voltage (V)	CIE ( $x$ , $y$ ) <sup>a</sup>
5	0.22, 0.22
6	0.26, 0.24
7	0.28, 0.26
8	0.28, 0.27
9	0.27, 0.27
10	0.26, 0.26
11	0.27, 0.27
12	0.27, 0.27

<sup>a</sup>Calculated from the EL spectrum.



absorption and emission spectra of PCPPV are red-shifted about 40–50 nm due to the vinylene units when compared with those of PCPP. The solid-state fluorescence spectrum is significantly broadened, and after annealing the film at 80 °C, the PL and EL emission spectra exhibited the quenching and aggregation effects, indicating that the increase in the interchain interactions of PCPPV, which gives effect to the  $\pi$ – $\pi^*$  transitions of the conjugated backbone, could be due to the aggregation caused by the planarity of the polymer in a polar solvent and solid state as a consequence of the phenanthrene and vinylene moieties. Since the low band gap polymers covering wide range of visible spectra are being investigated intensively for the purpose of improving the efficiency of the solar cell, the red-shifted derivatives with our conjugated backbone, bearing strong interchain interactions, may be useful for the polymer solar cells.

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