

Synthesis and Characterization of Novel Conjugated Polymer with 4*H*-Cyclopenta[*def*]phenanthrene and the Sulfanyl Group

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A novel 4*H*-cyclopenta[*def*]phenanthrene (CPP) derivative with bis-methylsulfanyl-methylene unit was synthesized from CPP, CH₃I, and CS₂. The structure and absolute configuration was determined on the basis of spectroscopic analyses and X-ray diffraction. New electroluminescent polymer with bis-methylsulfanyl-methylene unit in the PCPP backbone, poly-((2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene))-*alt*-(2,6-(4-(bis(methylsulfanyl)methylene)-4*H*-cyclopenta[*def*]phenanthrene))) (PCPP-MSC), have been synthesized by the Suzuki coupling reaction. The bis-methylsulfanyl-methylene unit was introduced on the PCPP backbone to affect a red-shifted color change and to increase the electron affinities of the polymer. The HOMO energy level of the polymer was -5.65 eV, and the LUMO energy level was -2.92 eV. The polymer, PCPP-MSC, using this CPP derivative exhibited absorption spectra with maximum peak at 341 nm in chlorobenzene solution and at 344 nm in the solid film state. The PCPP-MSC showed two PL emission peaks at 404 and 522 nm in chloroform solution with changing concentration. As concentration was growing from 1×10^{-8} mol/L to 1×10^{-5} mol/L, the PL peak at 522 nm increased dramatically, and the complete quenching of the host emission at 404 nm was observed, since complete aggregation between the cyclopentaphenanthrene segment and the methylsulfanylmethylene unit was induced by an intermolecular interaction.

KEY WORDS: Conjugated Polymer / 4*H*-cyclopenta[*def*]phenanthrene / Intermolecular Interaction / Optical Properties /

In the past few years, much research has been devoted to polymer light-emitting diodes (PLEDs) through the design and synthesis of light-emitting polymers for practical applications.¹ The color control and tuning of optical properties of conjugated polymers are important subject to achieve electroluminescence (EL) devices composed of these luminescent polymer materials. There are a few appropriate polymers for fabricating PLEDs that emit blue,² green,³ and red colors.⁴ Recently, red-emitting materials have been reported from the energy transfer between emissive polymers and several dyes, such as tetraphenylporphyrin and europium complexes.⁵ In this reason, the relation between the material structure was more important topic of discussion.

To design polymers with improved functional properties that cannot easily be attained by the corresponding homopolymers, considerable attention has been given to the syntheses and properties of conjugated copolymers in which the characteristics of the co-monomers possess a novel means.⁶ One of the keys in improvement of PLEDs is the discovery of the guest-host doped emitter system.⁷ A wide-band-gap host, with optimized transport and luminescent properties such as PFs, and a variety of highly fluorescent or phosphorescent narrow-band-gap guest dopants have been used to generate EL of desirable colors with very high efficiencies. New conjugated units containing sulfur, like 2,1,3-benzothiadiazole (BTs),⁸ have been investigated for use in red-light-emitting diodes.

Caused by the relatively high reduction potential and electron affinity, BTs are one of the most important moieties among the narrow-band-gap co-monomers. However, many light-emitting polymers with low electron affinities inject and transport holes due to their abundance of π -electrons.⁹ The strong electron-donor ability of these conjugated backbones have led to their application as a component of inter- and intramolecular charge-transfer systems.¹⁰ There are some reports about copolymers based on fluorene as a donor with various acceptor including BT. On the other hand, the monomer 4-(bis-methylsulfanyl-methylene)-4*H*-cyclopenta[*def*]phenanthrene (MSC) bearing only one bis-methylsulfanyl unit,¹¹ has received much less attention.

We have recently reported the synthesis of polycyclopentaphenanthrene (PCPP),¹² a new conjugated polymer previously investigated as a prospective blue emitting layer for PLEDs, given the stability of its thin film without any low-energy emission bands in the region of 500–600 nm even after annealing in air for 18 h at 150 °C or operation of the device in air for 40 min. The PLED based on PCPP generates EL emissions with high maximum brightness (1500 cd/m² at 14 V), high efficiency (0.70 cd/A at 180 mA/cm²), maximum peak at 400 nm, low turn-on voltage (6.0 V) and excellent CIE coordinates ($x = 0.17$, $y = 0.12$) for the blue color without any filtering. Emission color of PCPP can be changed over an entire visible region by introducing narrow-band-gap co-monomers

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into the PCPP backbone. In this work, we report on the synthesis, by Suzuki coupling, and characterization of the copolymer of 4*H*-cyclopenta[*def*]phenanthrene (CPP) and MSC. The MSC units were introduced into the main chains of PCPP for color tuning. The maximum peak of the PL spectra was at 545 and 649 nm. Devices based on this copolymer can emit red light with an emission maximum at 661 nm.

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. ^1H and ^{13}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. Flash column chromatography was performed with Merck silica gel 60 (particle size 230–400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) or fast atom bombardment (FAB) conditions in the Korea Basic Science Institute (Daegu, Korea). Elemental analyses (EA) were performed by Flash EA 1112 Series. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The thermal properties of this polymer was characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). T_g is temperature of transition of an amorphous or semi-crystalline polymer from a rubbery state to a glassy state. T_d is temperature at 5 wt % loss under nitrogen atmosphere. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermogravimetric analysis (TGA) was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 800 °C. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

Device Fabrication and Measurements

The UV-vis absorption spectra were recorded by a Varian Cary 1 spectrophotometer, while the Oriel InstaSpec IV CCD detection system with halogen lamp was used for the photoluminescence and electroluminescence spectra measurements. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT:PSS in aqueous isopropyl alcohol was spin-coated on the surface-

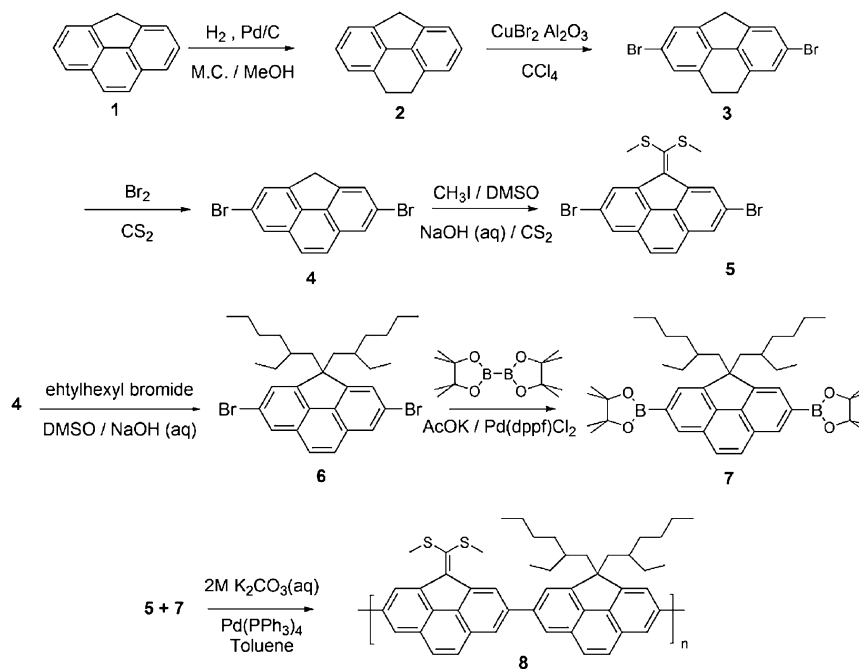
treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT:PSS layer, the emissive polymer film was obtained by spin casting chlorobenzene solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and Calcium electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm². For the determination of device characteristics, Current density-voltage (*J-V*) and luminance-voltage (*L-V*) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit equipped with a calibrated photomultiplier tube.

Synthesis of Monomers and Polymer

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (2). The mixture of 4*H*-cyclopenta[*def*]phenanthrene (**1**) (1.45 g, 7.62 mmol), 10% palladium-charcoal (300 mg), and methanol/dichloromethane (40 mL/40 mL) was shaken for 15 h at room temperature under a hydrogen atmosphere (60 psi). After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography to give 1.46 g (100%) of compound **2** as white solid: mp 134 °C; R_f 0.44 (SiO₂, 100% hexane) ^1H NMR (300 MHz, CDCl₃): δ (ppm) 3.18 (s, 4H), 3.92 (s, 2H), 7.17 (d, 2H, $J = 7.4$ Hz), 7.24 (t, 2H, $J = 7.4$ Hz), 7.37 (d, 2H, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CDCl₃): δ (ppm) 26.51, 37.69, 122.95, 124.92, 127.51, 130.76, 139.65, 140.67. HRMS (m/z , EI⁺) calcd for C₁₅H₁₂ 192.0939, found 192.0943.

2,6-Dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (3). To prepare copper bromide adsorbed on alumina, a solution of 10 g of copper bromide in 30 mL of distilled water was treated with neutral alumina (20 g, Merck aluminum oxide 90 active neutral) at room temperature. The reaction mixture was concentrated at 80 °C under reduced pressure. The resulting residue was dried under vacuum (4 Torr) at 100 °C for 15 h to generate the copper bromide adsorbed on alumina. To a stirred solution of 1.87 g (3.59 mmol) of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**) in 70 mL of carbon tetrachloride at room temperature was added 31.6 g of copper bromide adsorbed on alumina. After 5 h at 60 °C, the solid was filtered and washed with 2 × 30 mL of carbon tetrachloride. The combined organic phase was concentrated under reduced pressure and purified by flash column chromatography to give 3.36 g (99%) of compound **3** as pale yellow solid: mp 184 °C; R_f 0.50 (SiO₂, 100% hexane). ^1H NMR (300 MHz, CDCl₃): δ (ppm) 3.08 (s, 4H), 3.83 (s, 2H), 7.46 (s, 2H), 7.47 (s, 2H); ^{13}C NMR (75 MHz, CDCl₃): δ (ppm) 25.95, 37.35, 121.33, 126.43, 128.43, 131.91, 137.56, 141.81. HRMS (m/z , EI⁺) calcd for C₁₅H₁₀Br₂ 347.9149, found 347.9153.

2,6-Dibromo-4*H*-cyclopenta[*def*]phenanthrene (4). To a stirred solution of 3.15 g (9.1 mmol) of 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**3**) in 70 mL of carbon disulfide at room temperature was added dropwise 0.56 mL (10.8 mmol) of Br₂ in carbon disulfide over 3 h. The reaction mixture was stirred for 1 h, concentrated under reduced pressure, and



Scheme 1. Synthetic routes for PCPP-MS.

purified by flash column chromatography to give 3.15 g (100%) of compound **4** as pale yellow solid: mp 210 °C; R_f 0.53 (SiO₂, 100% hexane). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.32 (s, 2H), 7.75 (s, 2H), 7.80 (s, 2H), 7.99 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 37.16, 125.31, 125.62, 126.41, 127.97, 128.97, 132.91, 143.03. HRMS (m/z , EI⁺) calcd for C₁₅H₈Br₂ 345.8993, found 345.8993. Anal. Calcd for C₁₅H₁₀Br₂: C, 51.77; H, 2.32. Found: C, 52.60; H, 1.85.

4-Bis(methylsulfonyl)methylene-2,6-dibromo-4H-cyclopenta[def]phenanthrene (5). To a stirred solution of 9.16 g (26.3 mmol) of 2,6-dibromo-4H-cyclopenta[def]phenanthrene (**4**) and catalytic amounts of triethylbenzylammonium chloride in 500 mL of DMSO and 100 mL of CS₂ under nitrogen was added 9.8 mL (157.9 mmol) of iodomethane. After 1 h at 60 °C, 10 mL of 50% aqueous NaOH solution was added. The reaction mixture was cooled to room temperature and stirred for 5 h. After an excess amount of ethyl acetate was added, the organic layer was washed with 3 × 500 mL of water. The organic phase was dried with MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography to give 2.82 g (19.5%) of compound **5**, yellow powder: mp 191 °C; R_f 0.45 (SiO₂, methylene chloride:hexane = 1:10). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.82 (s, 6H), 7.27 (s, 2H), 7.95 (s, 2H), 8.82 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 18.25, 23.85, 121.87, 125.08, 126.42, 127.53, 127.94, 133.40, 136.54, 138.30. HRMS (m/z , EI⁺) calcd for C₁₈H₁₂Br₂S₂ 449.8747, found 449.8748. Anal. Calcd for C₁₈H₁₂Br₂S₂: C, 47.81; H, 2.67; S, 14.18. Found: C, 46.93; H, 2.54; S, 16.33.

2,6-Dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene (6). To a stirred solution of 3.12 g (8.9 mmol) of 2,6-dibromo-4H-cyclopenta[def]phenanthrene (**4**) and catalytic

amounts of triethylbenzylammonium chloride in 175 mL of DMSO under nitrogen was added 4.79 mL (27.0 mmol) of 2-ethylhexylbromide. After 1 h at 60 °C, 10 mL of 50% aqueous NaOH solution was added. The reaction mixture was cooled to room temperature and stirred for 5 h. After an excess amount of ethyl acetate was added to the reaction mixture, the organic layer was washed with 4 × 100 mL of water. The organic phase was dried with MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography to give 3.59 g (69.8%) of extremely clean compound **6**, white solid: mp 44 °C; R_f 0.65 (SiO₂, 100% hexane). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.49–0.85 (m, 30H), 2.12 (m, 4H), 7.66 (t, 2H, $J = 1.1$ Hz), 7.76 (s, 2H), 7.97 (d, 2H, $J = 1.1$ Hz); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 10.54, 14.20, 22.86, 27.55, 28.30, 34.08, 35.46, 44.04, 59.72, 121.86, 124.69, 125.63, 125.90, 128.64, 135.44, 150.96. HRMS (m/z , EI⁺) calcd for C₃₁H₄₀Br₂ 570.1497, found 570.1532. Anal. Calcd for C₃₁H₄₀Br₂: C, 65.04; H, 7.04. Found: C, 64.67; H, 7.41.

2-[4,4-Bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta[def]phenanthren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7). Under an argon atmosphere, 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene (**6**) (2.19 g, 3.8 mmol), bis(pinacolato)diboron (4.86 g, 19.2 mmol), AcOK (2.26 g, 22.9 mmol), and Pd(dppf)Cl₂ (0.18 g, 0.23 mmol) were dissolved in DMF (40 mL) and heated to 60 °C overnight. After the reaction mixture was cooled to room temperature, water and diethyl ether were added. The aqueous phase was extracted with diethyl ether and combined organic layer were dried over MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography to give 2.0 g (78%) of compound **7**, as

white solid: mp 97 °C; R_f 0.42 (SiO₂, ethyl acetate:hexane = 1:14). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.44–0.82 (m, 30H), 1.41 (s, 24H), 2.16 (d, 4H, J = 4.67 Hz), 7.94 (s, 1H by chirality of 2H), 7.96 (s, 2H by chirality of 2H), 7.98 (s, 1H by chirality of 2H), 8.31 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 10.61, 14.27, 22.90, 25.14, 27.73, 28.18, 33.98, 35.41, 44.03, 59.04, 83.91, 125.71, 126.04, 127.91, 128.23, 130.79, 139.71, 149.19. HRMS (m/z , FAB⁺) calcd for C₄₃H₆₄B₂O₄ 666.5005, found 666.4996.

Poly((2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene))-alt-(2,6-(4-(bis(methylsulfanyl)methylene)-4H-cyclopenta[def]phenanthrene))) (PCPP-MSC) (8). Carefully purified 2-[4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta[def]phenanthren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7) (544 mg, 0.8 mmol), 4-(bis(methylsulfanyl)methylene)-2,6-dibromo-4H-cyclopenta[def]phenanthrene (5) (369.7 mg, 0.8 mmol), and Pd(PPh₃)₄ (28.3 mg, 0.02 mmol) were dissolved in a mixture of toluene and aqueous 2 M K₂CO₃. The mixture was refluxed with vigorous stirring for 3 d under argon atmosphere. After the mixture was cooled to room temperature, it was poured into methanol. The precipitated material was recovered by filtration through a funnel. The resulting solid material was reprecipitated using methanol several times to remove catalyst residues. The obtained pale greenish-yellow solid was dried in vacuum to give 0.2 g: ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.80–0.87 (m, 26H), 1.61 (s, 6H), 2.11–2.21 (m, 4H), 2.44–2.76 (m, 4H), 7.32–8.22 (m, 10H), 9.18 (s, 2H). Anal. Calcd for C₄₉H₅₂S₂: C, 83.47; H, 7.43; S, 9.10. Found: C, 81.87; H, 6.60; S, 9.18.

RESULTS AND DISCUSSION

Synthesis and Characterizations

The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. In the first step, 4H-cyclopenta[def]phenanthrene (1) was hydrogenated using Pd/C to generate 8,9-dihydro-4H-cyclopenta[def]phenanthrene (2).¹³ Alumina-supported copper (II) bromide¹⁴ was used for the bromination to provide 2,6-bromo-8,9-dihydro-4H-cyclopenta[def]phenanthrene (3). 2,6-Dibromo-4H-cyclopenta[def]phenanthrene (4) was synthesized by dehydrogenation of compound 3 using bromine and carbon disulfide. After further alkylation of compound 4 with methyl iodide, the reaction, upon treatment with CS₂ in DMSO and 50% aqueous NaOH, led to compound 5,¹⁵ then analyzed using HRMS and NMR (500 MHz), including COSY, HMQC, and HMBC, as shown in Figure 1. In addition, the structure of a single crystal of compound 5, obtained from a CHCl₃/hexane solution, was confirmed by X-ray diffraction, as shown in Figure 2. Crystals of compound 5 belong to the triclinic system, space group P-1; a = 11.1829 (8), b = 11.5384 (8), c = 14.5606 (10), α = 109.7°, β = 103.3°, γ = 104.4°, Volume = 1609.04 (19) Å³, Z = 4, D_{calcd} = 1.867 Mg/m³, m = 5.290 mm⁻¹, $F(000)$ = 888. The final value of $R[I > 2\sigma(I)]$ was 0.0306, wR_2 = 0.0782, GooF = 1.062. Another monomer, 2-[4,4-bis(2-ethyl-

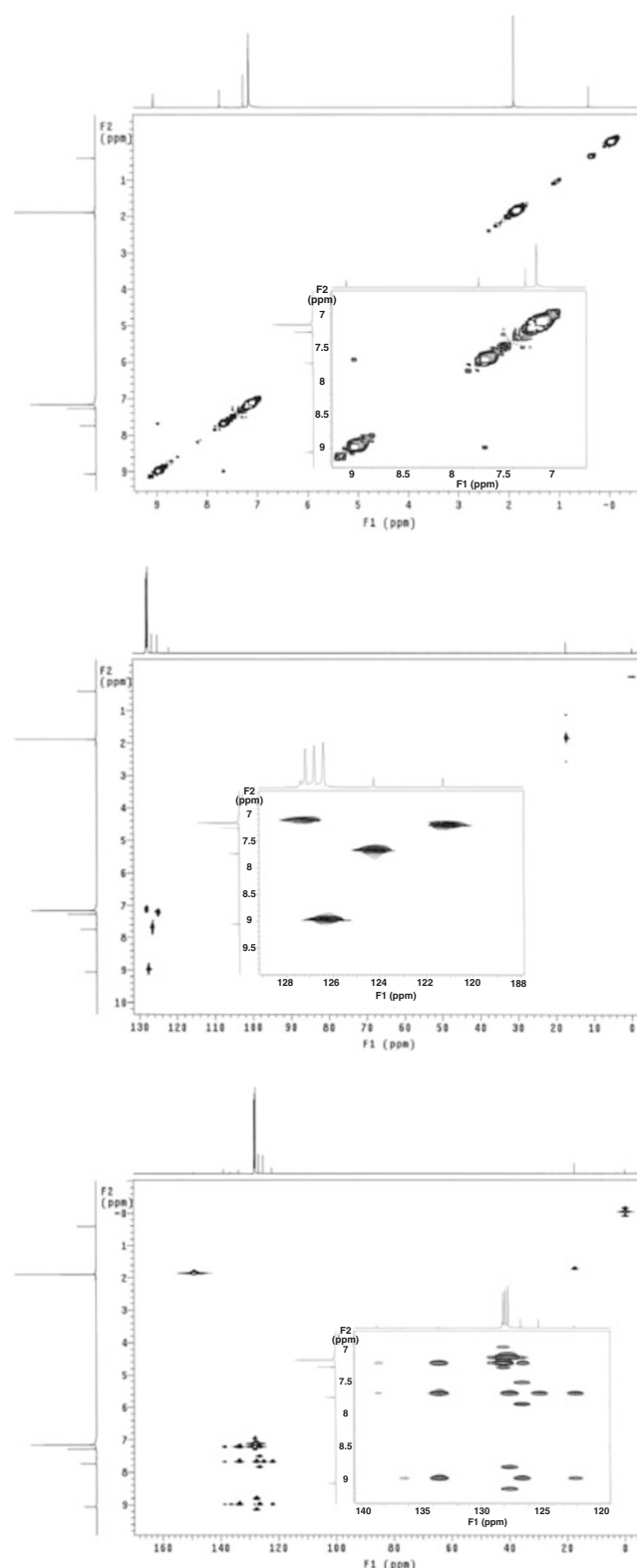


Figure 1. ¹H-¹H COSY, HMQC, and HMBC of compound 5.

hexyl)-6-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta[def]phenanthren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7) was synthesized by reacting compound 4 with 2-ethylhexylbromide, using catalytic amounts of triethylbenzyl

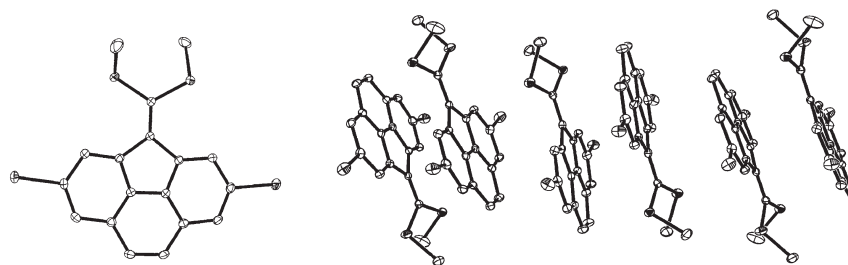


Figure 2. X-Ray structure and packing diagram of compound 5.

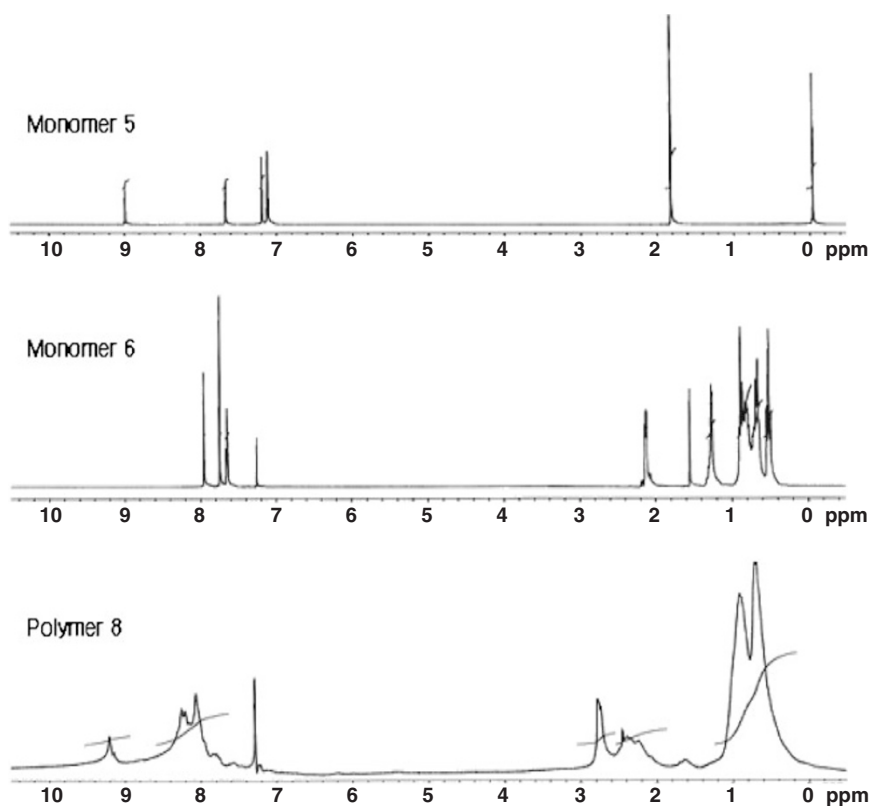


Figure 3. Comparison of ^1H NMR spectra of the polymer with those of monomeric compounds **5** and **6** in CDCl_3 .

ammonium chloride in DMSO and 50% aqueous NaOH, to obtain 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]-phenanthrene (**6**), which, upon reaction with bis(pinacolato)-diboron and catalytic amounts of $\text{Pd}(\text{dppf})\text{Cl}_2$ in DMF and potassium acetate, gave compound **7**. Suzuki coupling¹⁶ of monomer **5** and **7** using $\text{Pd}(\text{PPh}_3)_4$ and K_2CO_3 gave the final copolymer product, PCPP-MSC (**8**), ^1H NMR of which was compared with compound **5** and **6** in Figure 3.

The resulting PCPP-MSC was soluble in organic solvents such as chloroform, tetrahydrofuran, dichloromethane, and chlorobenzene. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the PCPP-MSC, determined by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the standard, was 10,400 and 17,700, respectively, with a polydispersity index in the range of 1.7. The thermal properties of the polymer was determined by DSC and thermal gravimetric analysis under a

nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. PCPP-MSC shows glass transition at 84°C and loses less than 5% of their weights on heating to 294°C (Figure 4). The high thermal stability of the resulting polymer prevents the deformation of the polymer morphology and degradation of the polymer light-emitting device by applied electric field of the LED.

Optical Properties of Polymer

As shown in Figure 5, PCPP-MSC showed an absorption spectrum with a maximum peak at 341 nm in chloroform. The film of the polymer was prepared by spin-casting from its chlorobenzene solution on a quartz substrate at room temperature, with the main absorption peak exhibited at 344 nm, attributed to the π - π^* transitions of the polymers. The polymer showed a different absorption spectrum side peak at 402 nm with the main bond at 344 nm. Compared with the spectrum of PCPP, the difference in shape was caused by the methylsulfa-

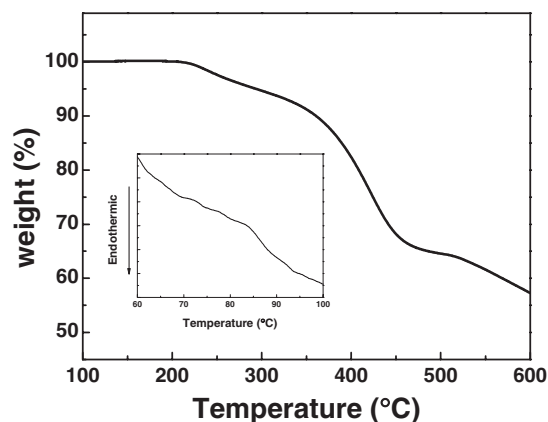


Figure 4. Thermogravimetric analysis of the PCPP-MSC under N_2 . Inner: Differential scanning calorimetry of the PCPP-MSC under N_2 .

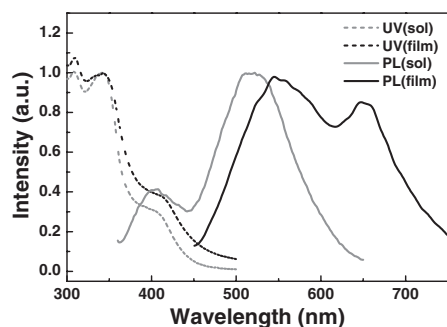


Figure 5. UV-vis absorption and photoluminescence emission spectra of PCPP-MSC in chloroform solution and in film.

nylmethylene units. The PL spectrum of the PCPP-MSC film showed a maximum at 545 nm and 649 nm with both the absorption and the emission spectra of the film red-shifted and broaden more than those in solution state, probably because of the increased intermolecular interactions due to methylsulfanylmethylene units between neighboring molecules in the film state. By this reason, the polymer exhibited the low absolute PL quantum yield of 0.12% in solution.

Figure 6 shows the PL spectra in chloroform at different concentrations for PCPP-MSC. At different concentrations, the polymer shows two PL emission peaks 404 and 522 nm. The PL peak at 522 nm increased dramatically with increasing solution concentration, however, complete quenching of the host emission at 404 nm was observed at a concentration of 1×10^{-5} mol/L, indicating complete aggregation between the cyclopentaphenanthrene segment and the methylsulfanylmethylene unit when an intermolecular interaction, by which the emission at around 400 nm responsible for the PCPP segment decreases very quickly with increasing copolymer concentration, takes place.

Electrochemical Properties of Polymer

The electrochemical properties of the polymer were determined from the band gap, estimated from the absorption edge, and the HOMO energy level, estimated using cyclic voltam-

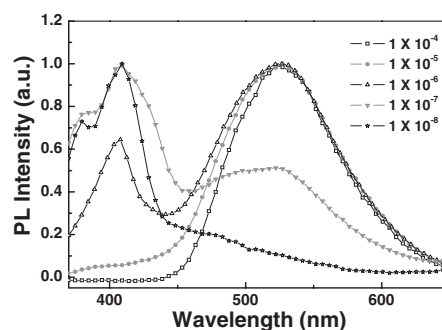


Figure 6. Photoluminescence spectra of PCPP-MSC in the chloroform solution at the concentration of 1×10^{-4} to 1×10^{-8} mol/L. The excitation wavelength is 340 nm.

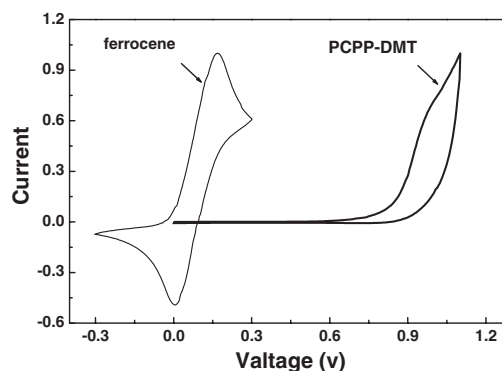


Figure 7. Cyclic voltammetry curves of the PCPP-MSC in 0.1 M Bu_4NBF_4 acetonitrile solution at a scan rate of 100 mV/s at room temperature (vs. an Ag quasi-reference electrode).

metry (CV) (Figure 7). The cyclic voltammograms were recorded using a voltammetric analyzer at room temperature under nitrogen atmosphere. The measuring cell consisted of polymer-coated Pt as working electrode, Ag/AgCl electrode as reference electrode, and platinum wire electrode as auxiliary electrode, supporting in 0.1 M $(n-Bu)_4NClO_4$ in acetonitrile. The energy levels were calculated using the ferrocene value of -4.8 eV with respect to vacuum level, which is defined as zero. The oxidation potential is derived from the onset of electrochemical p-doping, and HOMO level was calculated according to the empirical formula ($E_{HOMO} = -(E_{onset}]_{ox} + 4.8)$ (eV).¹⁷ In the anodic scan, the onset of oxidation of PCPP-MSC occurred at 0.85 V (vs. SCE), which corresponded to the ionization potential (I_p) value of -5.65 eV. The absorption onset wavelength of PCPP-MSC was observed at 454 nm for the solid thin film, corresponding to band gap of 2.73 eV. The LUMO energy level of the present PCPP-MSC, calculated from the values of the band gap and HOMO energy level, was -2.92 eV.

Electroluminescent Properties of Polymer

The electroluminescence (EL) spectrum of ITO/PEDOT/PCPP-MSC/Ca:Al device is shown in Figure 8. This spectrum exhibited maximum peak at 661 nm, corresponding to red light. The EL spectrum of the device using PCPP-MSC was very

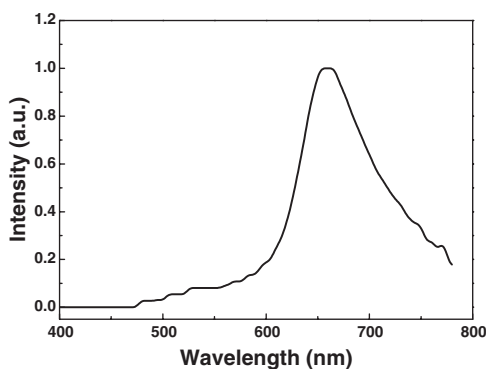


Figure 8. Electroluminescence spectrum of devices with the configuration of ITO/PEDOT:PSS/PCPP-MS-Ca:Al.

different from the PL spectrum, whose maximum peak at 545 nm in the film disappeared in the EL spectrum, which exhibited the poor luminous efficiency of 0.001 cd/A and the brightness of 0.434 cd/m². We can conclude that EL spectrum was red-shifted and the efficiency was decreased by aggregation between the PCPP segment and the methylsulfanyl-methylene units.

CONCLUSION

In conclusion, we presented the synthesis of a new CPP derivative, MSC, with bis-methylsulfanyl-methylene unit, which was analyzed by using HRMS and NMR (500 MHz), including COSY, HMQC, and HMBC, and was confirmed by X-ray diffraction. This molecule was introduced in a new conjugated polymer, PCPP-MS-Ca by the Suzuki coupling reaction. The bis-methylsulfanyl-methylene units affect a red-shifted color change and increase the electron affinities of the polymer. The HOMO energy level of the polymer was -5.65 eV, and the LUMO energy level was -2.92 eV. The PCPP-MS-Ca exhibited absorption spectra with maximum peak at 341 nm in chlorobenzene solution and at 344 nm in the solid film state. Its PL emission spectra in chloroform and in solid thin film showed maximum peaks at 404 and 522 nm, and at 524 and 649 nm, respectively. In a dilute chloroform solution, the PL peak at 522 nm increased dramatically and the PL peak at 404 nm was quenched completely with an increase in solution concentration. The complete aggregation between the cyclopentaphenanthrene segment and the methylsulfanyl-methylene unit was generated by an intermolecular interaction.

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