Articles

Alternating Aromatic and Transannular Chromophores with and without Linker: Effect of Transannular $\pi - \pi$ Interaction on the Optical Property of Dithiaparacyclophane-based Copolymers

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ABSTRACT: A series of bithiophene–cyclophane (PPP-type), acetylene–fluorene–acetylene–cyclophane (PPE-type), and ethylene–fluorene–ethylene–cyclophane (PPV-type) copolymers, namely, **4–6**, was synthesized via a nickel-catalyzed reaction, a palladium-catalyzed Sonagashira reaction, and a Heck coupling, respectively. Unlike in the fluorene–cyclophane copolymer **3**, the transannular π – π interaction of the cylophane unit in copolymer **4** resulted in a significant blue shift in its emission spectrum compared to a reference polymer, giving it an essentially blue emitting light. By introducing an acetylene or ethylene linker in going from **3** to **5** or **6**, the effective conjugation in the polymer backbone due to higher rigidity in coplanarity decreased the effect of the transannular π – π interaction. While the PPV-type copolymer **6** still exhibited an appreciable red shift in both absorption and emission with respect to a reference polymer, negligible shifts were observed for copolymer **5**.

Introduction

The broad applicability of conjugated polymers in light-emitting diodes,¹ field-effect transistors,² lightemitting electrochemical cells,³ solar cells,⁴ and sensors⁵ has attracted continuing interest in the design and synthesis of structurally diverse conjugated polymers that exhibit the various desired properties. Among the organic conjugated polymers, the properties of poly(pphenylenevinylenes) (PPVs) have been extensively studied and documented, ^{1a,6} while poly(*p*-phenylenes) (PPPs)⁷ and poly(p-phenyleneethynylenes) (PPEs)⁸ have also received considerable attention because of their favorable emission characteristics. Fluorene is one of the most universally employed building blocks in constructing conjugated copolymers that show blue-light-emitting characteristics. A large number of fluorene-based copolymers derived from comonomers such as benzenoids, thiophene, tertiary aromatic amine, benzothiadiazole, and benzooxadiazole were prepared by various synthetic coupling reactions.⁹ The PPV-type and PPE-type fluorene-based copolymers have also been explored¹⁰ in attempts to tune their spectral and electrical properties by incorporating various conjugated units into the polymer backbone.¹¹ The unique transannular $\pi - \pi$ interaction in [2.2]paracyclophane was employed in copolymers 1 that exhibited novel optical properties in comparison to the corresponding linear conjugated reference compounds.12 Our preliminary study of an example of copolymers 2, namely, the fluorene-dithia-

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[3.3]paracyclopane polymers 3a-c,¹³ showed that the transannular effect in the [3.3]cyclophane unit is sufficiently strong to allow tuning of the optical properties of copolymers 3a-c. [2.2]Paracyclophane-based polymers 1 are synthetically less accessible if functionalization on the cyclophane is desired. Dithia[3.3]paracyclophanes could, however, be readily prepared by coupling reactions under high dilution conditions.¹⁴ We report here a successful modulation in the optical properties of the bithiophene–dithia[3.3]paracyclophane copolymer 4 by the transannular effect of the [3.3]cyclophane unit. Additional effects derived from the introduction of a conjugated linker such as those in copolymers 5 and 6 were discussed in comparison to the properties of the parent copolymers 3.¹³



Experimental Section

General. All reactions were carried out under nitrogen. Commercially available reagents and solvents were used

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without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker ACF300 spectrometer in CDCl₃. EIMS and FAB-MS spectra were recorded using a Micromass 7034E mass spectrometer. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer for C, H, and S determination at the Chemical and Molecular Analysis Center, Department of Chemistry, National University of Singapore. GPC analyses were carried out using a Perkin-Elmer model 200 HPLC system calibrated using polystyrene as standard and THF as eluent. FT-IR spectra were recorded on a Bio-Red TFS 156 spectrometer. TGA was conducted on a DuPont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer in air or nitrogen. UV-vis and fluorescence spectra were obtained using a Shimadzu UV 3101PC UVvis-NIR spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as light source, respectively.

Synthesis. 1,4-Bis(methoxymethyl)-2,5-bis[2-(3-n-octylthienyl)/benzene (9a). A solution of 7 (3.24 g, 10 mmol) and 8 (24.25 g, 50 mmol) in DMF (60 mL) was carefully degassed by three freeze-thaw cycles, and the catalyst Pd(PPh₃)₄ (0.069 g, 0.06 mmol) was added. After the mixture was heated at 110 °C for 10 h, the solvent was removed under vacuum. The product was dissolved in diethyl ether, and the resulting solution was washed with aqueous 0.5 M KF, water, and brine and dried over sodium sulfate. The solvent was removed, and the residue was chromatographed on silica gel using hexane as eluent to give **9a** as colorless crystals (70%), mp 69–70 °C. ¹H NMR δ 7.44 (s, 2H), 7.28 (d, J = 5.1 Hz, 2H), 6.98 (d, J = 5.1 Hz, 2H), 4.32 (s, 4H), 3.29 (s, 6H), 2.40 (t, J = 7.7 Hz, 4H), 1.54–1.21 (m, 24H), 0.86 (t, J = 6.8 Hz, 6H). ¹³C NMR δ 140.20, 136.84, 134.62, 133.03, 131.01, 128.16, 124.13, 71.68, 58.16, 31.80, 30.53, 29.34, 29.16, 28.54, 22.59, 14.01. Anal. Calcd for C₃₄H₅₀S₂O₂: C, 73.59; H, 9.08; S, 11.56. Found: C, 73.42; H, 9.10; S, 11.28. MS (EI) m/z 554 (M+).

1,4-Bis(bromomethyl)-2,5-bis[2-(3-n-octylthienyl)]benzene (9b). HBr gas was bubbled vigorously through a solution of 9a (5.54 g, 10 mmol) in CHCl₃ (100 mL) for 1 h. The reaction mixture was then stirred for another 10 h, neutralized with 2 M NaHCO₃, and extracted with ether. The organic extracts were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed, and the residue was chromatographed on silica gel using hexane as eluent to give **9b** as a white solid (89%), mp 55–57 °C. ¹H NMR δ 7.45 (s, 2H), 7.34 (d, J = 4.9 Hz, 2H), 7.01 (d, J = 4.9 Hz, 2H), 4.41 (s, 4H), 2.43 (t, J = 7.8 Hz, 4H), 1.56–1.22 (m, 24H), 0.86 (t, J =6.6 Hz, 6H). $^{13}\mathrm{C}$ NMR δ 141.19, 137.53, 134.38, 132.96, 128.47, 124.82, 31.82, 30.63, 30.42, 29.33, 29.16, 28.69, 22.61, 14.05. Anal. Calcd for C₃₂H₄₄S₂Br₂: C, 58.89; H, 6.79; S, 9.83; Br, 24.49. Found: C, 58.97; H, 6.88; S, 9.79; Br, 24.28. MS (EI) m/z 650 (M⁺).

1,4-Bis(mercaptomethyl)-2,5-[2-(3-n-octylthienyl)]benzene (9c). A solution of 9b (6.52 g, 10 mmol) and thiourea (1.67 g, 22 mmol) in ethanol (100 mL) was slowly brought to reflux and heated for 6 h. The solvent was removed under reduced pressure. The dithiouronium salt was then refluxed in 4% aqueous NaHCO₃ for 3 h. The mixture was neutralized and extracted with ether and washed sequentially with water and brine. The combined organic extracts were dried over anhydrous sodium sulfate. The mixture was chromatographed on silica gel using hexane/ CH_2Cl_2 (4:1) as eluent to yield 9c as a yellow liquid (50%), mp 49-52 °C. ¹H NMR δ 7.35 (s, 2H), 7.31 (d, J = 5.2 Hz, 2H), 7.01 (d, J = 5.2 Hz, 2H), 3.63 (d, J = 8.0Hz, 4H), 2.43 (t, J = 7.7 Hz, 4H), 1.70 (t, J = 8.0 Hz, 2H), 1.55–1.23 (m, 24H), 0.87 (t, J = 6.8 Hz, 6H). ¹³C NMR δ 140.57, 139.66, 134.19, 133.44, 132.78, 128.43, 124.45, 31.83, 30.64, 29.35, 29.19, 28.70, 26.14, 22.62, 14.06. Anal. Calcd for C32H46S4: C, 68.76; H, 8.29; S, 22.95. Found: C, 68.99; H, 8.38; S, 23.10. MS (EI) m/z 558 (M⁺)

5,8-Bis[2-(3-n-octylthienyl)]-2,11-dithia[3.3]paracyclophane (11). A solution of 9c (1.67 g, 3.0 mmol) and 10 (0.79, 3.0 mmol) in degassed toluene was added dropwise with stirring to a solution of KOH (0.56 g, 10 mmol) and in ethanol (1 L). After the addition was completed, the reaction mixture was stirred for 20 h at room temperature. The solvent was removed, and the residue was chromatographed on silica gel using hexane/CH₂Cl₂ (4:1) as eluant to afford **11** as a white solid (30%), mp 105–106 °C. ¹H NMR δ 7.39 (d, J = 5.3 Hz, 2H), 7.24 (s, 2H), 7.19 (s, 4H), 7.01 (d, J = 5.3 Hz, 2H), 3.79 (d, J = 15.0 Hz, 2H), 3.78 (d, J = 15.0 Hz, 2H), 3.68 (d, J = 15.0 Hz, 4H), 2.41–2.31 (m, 2H), 2.17–2.07 (m, 2H), 1.46–1.11 (m, 24H), 0.82 (t, J = 7.0 Hz, 6H). ¹³C NMR δ 140.36, 135.70, 135.60, 135.06, 133.58, 132.61, 129.47, 129.36, 128.31, 124.30, 38.20, 34.90, 31.77, 30.12, 29.19, 28.58, 22.64, 14.08. Anal. Calcd for C₄₀H₅₂Sa: C, 72.67; H, 7.93; S, 19.40. Found: C, 72.79; H, 8.18; S, 19.69. MS (EI) *m/z* 660 (M⁺).

5,8-Bis[2-(5-bromo-3-n-octylthienyl)]-2,11-dithia[3.3]paracyclophane (12). A solution of Br₂ (0.4 g, 2.5 mmol) in AcOH/CHCl₃ was added dropwise to a solution of **11** (0.66 g, 1.0 mmol) in CHCl₃ cooled in an ice-water bath. The mixture was stirred for 24 h and extracted with CH₂Cl₂. The organic layer was washed with aqueous Na₂CO₃ and dried over Na₂SO₄. The crude product was chromatographed on a silica gel column using hexane as eluent to afford 12 as a white solid (72%), mp 131–133 °C. ¹H NMR δ 7.16 (s, 2H), 7.12 (s, 4H), 6.94 (s, 2H), 3.76 (d, J = 14.3 Hz, 2H), 3.75 (d, J = 15.2 Hz, 2H), 3.67 (d, J = 14.3 Hz, 2H), 3.63 (d, J = 15.2 Hz, 2H), 2.30-2.20 (m, 2H), 2.05-1.95 (m, 2H), 1.35-0.96 (m, 24H), 0.83 (t, J = 7.0 Hz, 6H). ¹³C NMR δ 141.12, 136.89, 135.77, 135.28, 133.57, 131.89, 131.02, 129.44, 129.24, 111.13, 38.16, 34.72, 31.69, 29.85, 29.07, 29.01, 28.50, 22.57, 14.00. Anal. Calcd for C40H50Br2S4: C, 58.67; H, 6.15; S, 15.66; Br, 19.51. Found: C, 58.72; H, 6.24; S, 15.78; Br, 19.34. MS (EI) m/z 816 (M+).

1,4-Dimethyl-2,5-bis/2-(3-n-octylthienyl)/benzene (14). A solution of 8 (24.25 g, 50 mmol) and 13 (2.64 g, 10 mmol) in DMF (60 mL) was carefully degassed by three freeze-thaw cycles, and $Pd(PPh_3)_4$ (0.069 g, 0.06 mmol) was added. After the mixture was heated at 110 $^\circ C$ for 10 h, the solvent was removed under vacuum. The product was dissolved in diethyl ether, and the resulting solution was washed with aqueous 0.5 M KF, water, and brine and dried over sodium sulfate. The solvent was removed, and the residue was chromatographed on silica gel using hexane as eluent to give 14 as a white solid (65%). ¹H NMR δ 7.24 (s, 2H), 7.12 (d, J = 5.4 Hz, 2H), 6.72 (d, J = 5.4 Hz, 2H), 2.57 (t, J = 7.8 Hz, 4H), 2.37 (s, 6H), 1.65–1.24 (m, 24H), 0.90 (t, J = 6.6 Hz, 6H). ¹³C NMR δ 138.83, 137.31, 133.72, 130.60, 130.29, 128.17, 125.82, 33.40, 30.95, 29.44, 29.34, 29.19, 28.69, 22.61, 14.67, 14.02. Anal. Calcd for C₃₂H₄₆S₂: C, 77.67; H, 9.37; S, 12.96. Found: C, 77.31; H, 9.25; S, 12.74. MS (EI) m/z 504 (M+).

1,4-Bis[2-(5-bromo-3-n-octylthienyl)]-2,5-dimethylbenzene (**15**). This was prepared by a similar procedure as described for **12**. ¹H NMR δ 7.22 (s, 2H), 6.77 (s, 2H), 2.56 (t, J = 7.8 Hz, 4H), 2.36 (s, 6H), 1.62–1.28 (m, 24H), 0.91 (t, J = 6.6 Hz, 6H). ¹³C NMR δ 140.01, 137.11, 135.14, 133.96, 132.68, 129.68, 111.04, 32.87, 30.84, 29.93, 29.36, 29.23, 28.66, 22.69, 14.69, 14.13. Anal. Calcd for C₃₂H₄₄S₂Br₂: C, 58.89; H, 6.79; S, 9.83, Br, 24.48. Found: C, 59.04; H, 7.04; S, 9.97, Br, 24.67. MS (EI) m/z 650 (M⁺).

General Procedure for the Preparation of Polymers 4 and 16. 12 or 15 (10 mmol), anhydrous $NiCl_2$ (0.75 mmol), PPh₃ (10 mmol), 2,2'-bipyridine (0.75 mmol), and zinc powder (31 mmol) were mixed, degassed thoroughly, and maintained under argon. DMF (15 mL) was added, and the reaction mixture was stirred at 85 °C for 20 h. The mixture was cooled to room temperature and extracted with CHCl₃. The organic layer was poured into cold methanol. The yellow solid precipitated was collected by filtration. The solid was washed for 24 h in a Soxhlet apparatus using acetone. The soluble polymer was extracted with chloroform from the residue in the Soxhlet apparatus.

Polymer **4**. Yield: 66%. ¹H NMR δ 7.35–7.25 (br, m), 3.88– 3.74 (br, m) 2.40–2.03 (br, m), 1.67–1.18 (br, m), 0.86–0.84 (br, m). Anal. Calcd for (C₄₀H₅₀S₄)_n: C, 72.89; H, 7.65; S, 19.46. Found: C, 71.46; H, 7.90; S, 18.59.

Polymer **16.** Yield: 75%. ¹H NMR δ 7.36–6.98 (br, m), 2.73–2.64 (br, m), 2.24 (br, s), 1.68–1.27 (br, m), 0.88–0.86 (br, m); Anal. Calcd for $(C_{32}H_{44}S_2)_n$: C, 95.10; H, 10.97; S, 15.87. Found: C, 94.57; H, 10.47; S, 15.48.

Synthesis. 9,9-Di-n-hexyl-2,7-bis[(trimethylsilyl)ethylnyl]fluorene (18). A solution of trimethylsilyl acetylene (1.08 g, 11 mmol) in triethylamine (20 mL) was slowly added to a solution of 17 (2.46 g, 5.0 mmol), (Ph₃P)₂PdCl₂ (0.175 g, 0.25 mmol), and CuI (0.047 g, 0.25 mmol) in triethylamine (50 mL) under nitrogen at room temperature. The reaction mixture was then stirred at 70 °C for 8 h. The solvent was then removed under reduced pressure, and the residue was chromatographed on silica gel using hexane as eluent to give 18 as a yellow solid (62%), mp 121–123 °C. ¹H NMR δ 7.58 (d, J = 7.3 Hz, 2H), 7.45 (dd, J = 8.0 Hz, 1.0 Hz, 2H), 7.41 (s, 2H), 1.95–1.90 (m, 4H), 1.13-1.01 (m, 12H), 0.76 (t, J = 7.0 Hz, 6H), 0.53-0.51(m, 4H), 0.28 (s, 18H). 13 C NMR δ 150.91, 140.81, 131.18, 126.18, 121.73, 119.76, 106.06, 94.21, 55.19, 40.31, 31.49, 29.64, 23.58, 22.56, 13.92. Anal. Calcd for C₃₅H₅₀Si₂: C, 79.78; H, 9.56. Found: C, 80.07; H, 9.59. MS (EI) m/z 526 (M⁺).

2,7-Diethynyl-9,9-di-n-hexylfluorene (**19**). An aqueous KOH solution (6 mL, 20%) was diluted with methanol (25 mL) and added to a stirred solution of **18** (2.63 g, 5 mmol) in THF (50 mL). The mixture was stirred at room temperature for 6 h and extracted with hexane. The organic fraction was washed with water and dried over sodium sulfate. The crude product was chromatographed on silica gel using hexane as eluent. Recrystallization of the product from methanol gave **19** as yellow crystals (80%), mp 35.0–35.4 °C. ¹H NMR δ 7.63 (d, J = 7.7 Hz, 2H), 7.47 (dd, J = 7.7 Hz, 1.4 Hz, 2H), 7.45 (s, 2H), 3.15 (s, 2H), 1.96–1.90 (m, 4H), 1.14–1.01 (m, 12H), 0.76 (t, J = 7.0 Hz, 6H), 0.58–0.53 (m, 4H). ¹³C NMR δ 151.02, 140.95, 131.21, 126.51, 120.81, 119.92, 84.49, 55.17, 40.19, 31.44, 29.58, 23.62, 22.52, 13.91. Anal. Calcd for C₂₉H₃₄: C, 91.04; H, 8.96. Found: C, 91.58; H, 8.89. MS (EI) *m/z* 382 (M⁺).

General Procedure for the Preparation of Polymers 5a–c and 21. 2,7-Diethynyl-9,9-dihexylfluorene 19 (191 mg, 0.5 mmol), monomer $20a-c^{13}$ or 2,5-dibromo-*p*-xylene 13 (0.5 mmol), (Ph₃P)₂PdCl₂ (35 mg, 0.03 mmol), and CuI (28 mg, 0.15 mmol) were added to a mixture of degassed toluene (14 mL) and diisopropylamine (6 mL). The mixture was vigorously stirred at 70 °C for 24 h under nitrogen. After the mixture was cooled to room temperature, it was extracted with chloroform. The combined organic extracts were poured slowly into cold methanol. The precipitated solid was washed with methanol, water, and methanol successively. The product was further washed with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues. The polymer was then dried under vacuum at room temperature.

Polymer **5a**. Yield: 75%; a fibrous yellow solid. ¹H NMR δ 7.56 (br, s), 7.17 (br, s), 4.48 (br, d), 4.17 (br, d), 3.88 (br, s), 3.69 (br, d), 2.03 (br, s), 1.26–0.79 (br, m). FT-IR (KBr) 3053, 2926, 2852, 1602, 1462, 1419, 1373, 1257, 1101, 889, 743 cm⁻¹. Anal. Calcd for $(C_{43}H_{46}S_2)_n$: C, 82.38; H, 7.39. Found: C, 81.03; H, 7.24.

Polymer **5b**. Yield: 68%; a fibrous yellow solid. ¹H NMR δ 7.80–7.60 (br, m), 7.48–7.45 (br, m), 7.35–7.16 (br, m), 6.95–6.50 (br, m), 4.31–3.19 (br, m), 3.90 (br, s), 2.04–1.97 (br, m), 1.25–0.71 (br, m). FT-IR (KBr) 3059, 2957, 2926, 2851, 1607, 1462, 1395, 1207, 1043, 870, 654 cm⁻¹. Anal. Calcd for ($C_{45}H_{50}S_2O_2$)_n: C, 78.67; H, 7.34. Found: C, 78.04; H, 7.12.

Polymer **5***c*. Yield: 62%; a fibrous green solid. ¹H NMR δ 7.68–7.53 (br, m), 3.87 (br, s), 1.99 (br, s), 1.59–1.09 (br, m), 0.78 (br, s). FT-IR (KBr) 3057, 2926, 2853, 2205, 1604, 1462, 1377, 1261, 1095, 1024, 896, 817, 692, 520 cm⁻¹. Anal. Calcd for $(C_{45}H_{44}S_2N_2)_n$: C, 79.84; H, 6.55; N, 4.14. Found: C, 78.32; H, 6.70; N, 4.05.

Polymer **21**. Yield: 75%; a fibrous green solid. ¹H NMR δ 7.68 (br, s), 7.52–7.50 (br, m), 7.43–7.40(br, m), 2.54–2.36 (br, m), 1.99 (br, s), 1.07–0.64 (br, m). FT-IR (KBr) 3059, 3030, 2926, 2827, 1600, 1491, 1462, 1377, 1260, 1095, 1019, 887, 820, 721, 528 cm⁻¹. Anal. Calcd for $(C_{35}H_{40})_n$: C, 91.25; H, 8.75. Found: C, 90.01; H, 8.87.

Synthesis. 2, 7-Diformyl-9,9-di-n-hexylfluorene (**22**). A solution of *n*-BuLi (1.60 M, 20.5 mmol) was added dropwise under nitrogen to a cooled (-78 °C) solution of **17** (4.92 g, 10 mmol) in dry THF (70 mL). The resulting mixture was stirred at -78 °C for 1 h, and a mixture of dry DMF (2.5 mL) and dry THF (20 mL) was added. The reaction mixture was stirred at room

temperature for 18 h. The solvent was removed in vacuo, and the residue was extracted with ether. The organic layer was washed with water and dried over Na₂SO₄. The crude product was chromatographed on silica gel using hexane/ethyl acetate (20:1) as eluent to give **22** as a light yellow solid (51%), mp 52-54 °C. ¹H NMR δ 10.08 (s, 2H), 7.93-7.87 (m, 6H), 2.08-2.03 (m, 4H), 1.07-0.98 (m, 12H), 0.69 (t, J = 6.8 Hz, 6H), 0.54-0.48 (m, 4H). ¹³C NMR δ 192.06, 152.83, 145.58, 136.43, 130.21, 123.38, 121.29, 55.53, 39.97, 31.35, 29.43, 23.72, 22.41, 13.86. Anal. Calcd for C₂₇H₃₄O₂: C, 83.03; H, 8.77. Found: C, 82.74; H, 8.51; MS (EI) *m/z* 390 (M⁺).

9,9-Di-n-hexyl-2,7-bis(hydroxymethyl)fluorene (**23a**). To a solution of **22** (3.90 g, 10 mmol) in ethanol (50 mL) was added NaBH₄ (0.38 g, 10 mmol). The mixture was stirred at room temperature for 6 h, and the solvent was removed to yield an oily residue. The crude product was chromatographed on silica gel using CH₂Cl₂ as eluent to give **23a** as a light yellow oil (93%). ¹H NMR δ 7.66 (dd, J = 7.32 Hz, J = 1.05 Hz, 2H), 7.33 (s, 2H), 7.32 (d, J = 7.29 Hz, 2H), 4.77 (s, 4H), 1.98–1.92 (m, 4H), 1.14–1.02 (m, 12H), 0.75 (t, J = 7.0 Hz, 6H), 0.62–0.60 (m, 4H). ¹³C NMR δ 151.34, 140.38, 139.79, 125.73, 121.51, 119.63, 65.72, 55.01, 40.30, 31.45, 29.66, 23.73, 22.54, 13.93. Anal. Calcd for C₂₇H₃₆O₂: C, 82.61; H, 9.24. Found: C, 82.51; H, 9.60; MS (EI) *m/z* 392 (M⁺).

2,7-Bis(chloromethyl)-9,9-di-n-hexylfluorene (**23b**). To a solution of **23a** (3.92 g, 10 mmol) in benzene (30 mL) was added a solution of SOCl₂ (3.57 g, 30 mmol) in benzene (10 mL). The mixture was heated at 50 °C for 4 h. The reaction mixture was cooled to room temperature, consecutively washed with saturated aqueous NaHCO₃ an H₂O, and dried over Na₂SO₄. The solvent was removed, and the crude product was chormatographed on silica gel using hexane as eluent to give **23b** as a colorless oil (85%). ¹H NMR δ 7.66 (d, J = 7.3 Hz, 2H), 7.35 (d, J = 7.3 Hz, 2H), 7.34 (s, 2H), 4.68 (s, 4H), 1.97–1.92 (m, 4H), 1.14–1.04 (m, 12H), 0.76 (t, J = 6.8 Hz, 6H), 0.62–0.60 (m, 4H). ¹³C NMR δ 151.61, 140.78, 136.60, 127.56, 123.22, 120.01, 55.18, 46.86, 40.15, 31.40, 29.59, 23.69, 22.53, 14.00. Anal. Calcd for C₂₇H₃₄Cl₂: C, 75.51; H, 7.98; Cl, 16.51. Found: C, 75.27; H, 7.95; Cl, 16.30. MS (EI) *m/z* 428 (M⁺).

9,9-Di-n-hexyl-2,7-bis(triphenylphosphoniomethyl)fluorene dichloride (**23c**). A mixture of **23b** (4.29 g, 10 mmol) and Ph₃P (5.77 g, 22 mmol) in DMF (35 mL) was stirred at 100 °C for 5 h. The reaction mixture was cooled to room temperature and poured into dry diethyl ether (400 mL). The precipitate was collected by filtration and recrystallized from ethanol to afford **23c** as a white solid (90%), mp 333–338 °C. ¹H NMR δ 7.70–7.60 (m, 30H), 7.37 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 7.7 Hz, 2H), 6.94 (s, 2H), 5.48 (d, J = 14.3 Hz, 4H), 1.78–1.47 (m, 4H), 1.11–0.75 (m, 18 H), 0.22–0.20 (m, 4H). ¹³C NMR δ 151.28, 140.46, 134.88, 134.43, 134.29, 130.84, 130.18, 130.01, 126.42, 126.30, 125.29, 120.36, 118.61, 117.47, 58.41, 54.90, 39.97, 31.73, 31.60, 30.98, 29.64, 23.86, 22.69, 18.37, 14.05. Anal. Calcd for C₆₃H₆₄Cl₂P₂: C, 79.33; H, 6.72. Found: C, 79.04; H, 6.64. MS (FAB): 952 (M⁺).

2,7-Diethenyl-9,9-di-n-hexylfluorene (23d). An aqueous solution of NaOH (2.5 g/15 mL water) was added to a mixture of 23c (6.91 g, 10 mmol) and aqueous formaldehyde (37%, 30 mL) in water (15 mL). The resulting solution was stirred at room temperature for 18 h, and the mixture was extracted with ether. The organic layer was separated, washed with water and brine, and then dried over anhydrous sodium sulfate. The crude product was chromatographed on silica gel using hexane as eluent to give 23d as a colorless oil (86%). ¹H NMR δ 7.71 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.48 (s, 2H), 6.90 (dd, J = 17.4 Hz, 10.8 Hz, 2H), 5.89 (d, J = 17.4 Hz, 2H), 5.34 (d, J = 10.8 Hz, 2H), 2.13–2.08 (m, 4H), 1.23–1.17 (m, 12H), 0.87 (t, J = 6.8 Hz, 6H), 0.80–0.77 (m, 4H). ¹³C NMR δ 151.43, 140.85, 137.51, 136.65, 125.35, 120.58, 119.77, 112.96, 54.99, 40.55, 31.70, 31.55, 29.80, 23.80, 22.75, 22.66, 14.17, 14.03. Anal. Calcd for C₂₉H₃₈: C, 90.09; H, 9.91. Found: C, 89.93; H, 9.98. MS (EI) m/z 386 (M⁺).

General Procedure for the Preparation of Polymers 6 and 24. A mixture of **20a** (1.0 mmol) or **13**, **23d** (0.386 g, 1.0 mmol), Pd(OAc)₂ (0.009 g, 0.04 mmol), tri-*o*-tolylphosphine (0.061 g, 0.2 mmol), and tributylamine (0.5 mL) in DMF (10

mL) was heated at reflux under nitrogen for 2 days. The mixture was poured into cold methanol (200 mL), and the precipitate was collected by filtration. The product was redissolved in a minimum volume of THF and reprecipitated by adding the THF solution dropwise into cold methanol. The resulting solid was washed with methanol and acetone and then extracted by chloroform in a Soxhlet extractor. The desired polymer was isolated after removal of chloroform under reduced pressure. The polymer was then dried under vacuum.

Polymer **6**. Yield: 30%; a yellow-green solid. ¹H NMR δ 7.75 (br, 2H), 7.61 (br, 2H), 7.54 (br, 2H), 7.51 (br, 2H), 7.47–7.42 (br, 2H), 7.18–7.00(br, 6H), 2.04–0.76 (br, 26H). FT-IR (KBr) 3085, 3006, 2926, 2857, 1678, 1604, 1464, 1356, 1259, 1097, 1043, 896, 869 cm⁻¹. Anal. Calcd for $(C_{45}H_{50}S_2)_n$: C, 82.57; H, 7.65. Found: C, 82.01; H, 7.21.

Polymer **24.** Yield: 63%; a yellow-green solid. ¹H NMR δ 7.70 (br, 2H), 7.57 (br, 2H), 7.51 (br, 2H), 7.47 (br, 2H), 7.42–7.37 (br, 2H), 7.19–7.13 (br, 2H), 2.58 (br, 6H), 2.04–0.76 (br, 26H). FT-IR (KBr) 3015, 2924, 2852, 1676, 1598, 1491, 1460, 1375, 1255, 1028, 956, 881, 808, 746 cm⁻¹. Anal. Calcd for (C₃₇H₄₄)_n: C, 90.93; H, 9.07. Found: C, 90.09; H, 8.59.



Results and Discussion

Synthesis of Monomers and Polymers. The general synthetic route to polymer 4 and its reference polymer 16 is outlined in Scheme 1. The palladiumcatalyzed coupling reaction between 7 and 2-tri-nbutylstannyl-3-n-octylthiophene 8 afforded compound 9a. Treatment of 9a with HBr in chloroform gave the desired dibromide 9b, which reacted with thiourea followed by base hydrolysis to afford the dithiol 9c. The coupling reaction between 9c and 1,4-bis(bromomethyl)benzene 10 under high dilution conditions afforded the desired dithia[3.3]paracyclophane 11. Bromination of 11 with bromine in CHCl₃/AcOH (1:1) afforded the dibromo monomer 12. Similarly, the palladium-catalyzed coupling reaction between 8 and 13 gave compound 14, which upon bromination led to the dibromo monomer 15. Polymerization of 12 or 15 was achieved according to the literature method.¹⁵ The polymers 4 and 16 were obtained in yields of 66% and 75%, respectively.

The synthetic route to the monomers and the corresponding copolymers $5\mathbf{a}-\mathbf{c}$ and $\mathbf{6}$ is shown in Schemes 2 and 3, respectively. The key monomer 2,7-diethynyl-

Scheme 1. Synthesis of Polymers 4 and 16^a



^a Reagents and conditions: (i) Pd(PPh₃)₄/DMF, 110 °C; (ii) HBr/CHCl₃, room temperature; (iii) NH₂C(S)NH₂/ethanol/NaHCO₃, reflux; (iv) KOH/Cs₂CO₃/ethanol/toluene, high dilution conditions; (v) Br₂/CHCl₃/AcOH, room temperature; (vi) anhydrous NiCl₂/PPh₃/2,2'-bipyridine/Zn powder/DMF, 85 °C.

Scheme 2. Synthesis of Polymers 5 and 21^a



^{*a*} Reagents and conditions: (i) $(PPh_3)_2PdCl_2/CuI/(CH_3)_3SiC \equiv CH/(Et)_3N$, 70 °C; (ii) $CH_3OH/THF/KOH$, room temperature; (iii) $Pd(PPh_3)_4/CuI/diisopropylamine/toluene$, 70 °C.

9,9-di-*n*-hexylfluorene **19** was prepared from a palladium(II)-catalyzed Sonagashira cross-coupling reaction between 2,7-dibromo-9,9-dihexylfluorene **17** and trimethylsilyl acetylene followed by subsequent removal of the trimethylsilyl protecting group upon base treatment.¹⁶ The dithiaparacyclophanes **20a**-**c** were prepared by coupling the corresponding pair of dithiol and dibromide under high dilution conditions.¹³ The pal-





^{*a*} Reagents and conditions: (i) DMF/n-BuLi/THF; (ii) NaBH₄/ ethanol, room temperature; (iii) SOCl₂/benzene, 50 °C; (iv) PPh₃/DMF, 100 °C; (v) 37% formaldehyde/NaOH, room temperature; (vi) tri-*o*-tolylphosphine/Pd(OAc)₂/DMF/Bu₃N, 160 °C.

ladium-catalyzed cross-coupling condensation reactions¹⁷ leading to the PPE-type copolymers 5a-c and 21 proceeded well between 20a-c or 13 and 19. The copolymers 5a-c were isolated in good yields of 62– 75%. Polymers 5a and 5b were isolated as yellow solids, while 5c and 21 were green solids.

The bis(organolithium) compound prepared from dibromo 17 and n-BuLi reacted readily with DMF to afford the dialdehyde 22. Reduction of 22 with NaBH₄ followed by treatment with SOCl₂ gave the dichloro compound **23b**, which formed the bis(phosphonium) salt 23c with triphenylphosphine. A Wittig reaction between **23c** and formaldehyde gave the divinyl monomer **23d**. The PPV-type copolymers 6 and 24 were prepared from Heck reactions¹⁸ between **23d** and **20a** or **13**, respectively.¹⁹ Our attempts to modify the experimental parameters led to reasonable yields (30% and 63%, respectively) for the desired polymers 6 and 24 when reactions were carried out in DMF at reflux for 48 h. Due to the high reaction temperature employed, tri-*n*butylamine with a higher boiling point was used to replace the more commonly used tri-n-ethylamine to prevent loss of the base during the reaction.

The structures of all polymers prepared in our work were characterized by ¹H NMR spectroscopic and element analyses. Figure 1 illustrates two representative ¹H NMR spectra of polymers **4** and **5a**. In the ¹H NMR spectrum of 5a, for example, the signals appearing in the range of δ 7.64–7.50 correspond to those in fluorene while those at δ 7.22–7.15 are assigned to those in the paracyclophane. The multiplets at δ 3.69–4.48 are characteristic of benzylic protons of dithiacyclophanes, indicating that the paracyclophane units remain intact during the polymerization. Figure 2 shows the wideangle X-ray diffraction patterns of copolymers 5a-c. Unlike the linear PPEs²⁰ which are semicrystalline and exhibit a lamellar structure, the polymers 5a-c display predominantly an amorphous phase. The introduction of the paracyclophane units in these polymers may be responsible for the relatively less-ordered packing of polymer chains.

All polymers prepared in our work were readily soluble in common organic solvents such as THF, chloroform, toluene, and xylenes. The molecular weights of the polymers determined by gel permeation chromatography (GPC) against the polystyrene standards are



Figure 1. ¹H NMR spectra of (a) **4** and (b) **5a** in CDCl₃ (asterisk (*) indicates residual water and CHCl₃).



Figure 2. Powder X-ray diffraction pattern of copolymers 5a-c.

 Table 1. Molecular Weights, Product Yields, and Thermal Analysis Data of Polymers 4–6, 16, 21, and 24

	U	v			
polymer	$M_{ m n}$	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$	yield (%)	$T_{\rm d}$ (°C)
4	4 100	7 000	1.70	66	322
16	31 400	38 100	1.21	75	409
5a	56 700	88 600	1.56	75	330
5b	48 500	77 200	1.59	68	288
5c	43 300	76 400	1.76	62	256
21	44 800	82 800	1.84	75	382
6	3 300	5 900	1.78	30	300
24	3 600	6 900	1.91	63	400

summarized in Table 1. Thermal stability of the polymers was investigated by thermogravimetric analysis (TGA). The PPE-type copolymers **5a**-**c** showed inferior thermal stability to the reference polymer **21** possibly due to desulfurization of the dithiaparacyclophane moiety. A decrease in decomposition temperature (T_d) going from 16 to 4 and 24 to 6 was also observed possibly due to a similar reason. The glass phase transition of all the dithiaparacyclophane-based copolymers was not noticeable by differential scanning calorimetry. The molecular weight of polymers 5a-c with a polydiversity in the range of 1.56-1.76 was about 43 000 and higher. Those of 4 and 6 were, however, very much lower at 3300-4100. This could be a result of the more efficient Songashira reaction compared to the Heck and nickel(0)-catalyzed coupling reactions.

Table 2. Optical Data and Fluorescence Quantum Yieldof Polymers 3-6, 16, 21, 24, and 25

	$\lambda_{\max}(\text{THF})^a$ (nm)		$\lambda_{\max}(\text{film})^a$ (nm)		
polymer	abs	em	abs	em	$\phi_{\mathrm{F}}{}^{b}$
3a	361	411 (428)	367	417 (440)	0.75
25	330	376	333	385	0.50
4	374	441	374	454	0.17
16	344	469	350	480	0.15
5a	378 (408)	471 (427, 448)	386 (410)	484 (515)	0.22
5b	384 (411)	471 (426, 500)	388 (424)	492 (518)	0.16
5c	385 (408)	471 (429, 503)	390 (416)	479	0.15
21	379 (402)	468 (423, 443)	384	478 (523)	0.24
6	400	461 (445)	403	476 (444, 504, 535)	0.21
24	390	450 (483)	395	464 (495)	0.49

 a Data in parentheses are wavelengths of shoulders and subpeaks. b The ϕ_F of the polymer in a THF solution was measured by using quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4 , assuming ϕ_F of 0.55) as a standard.



Figure 3. UV–vis absorption and fluorescence spectra of **4** and **16** measured from solutions (ca. 1×10^{-5} M) in THF at room temperature.

Optical Properties. The spectroscopic properties of the polymers prepared in this work were determined both in solution (THF) and as a thin film. Their optical properties are summarized in Table 2. Transparent and uniform films of the polymers were prepared on guartz by spin-casting their solutions in chloroform at room temperature. In our earlier report,¹³ a significant red shift was observed going from the reference polymer 25 to the cyclophane-based polymer 3a (Table 2) resulting from the transannular $\pi - \pi$ interaction in the cyclophane unit. Changing the aromatic chromophore from fluorene in **3a** to bithiophene in **4**, however, led to a very different observation (Table 2; Figure 3). In comparison to the reference polymer 16, the cyclophane-based polymer 4 exhibited a significant absorption red shift by 30 nm but its emission λ_{max} was unexpectedly blueshifted by 28 nm. In fact, such a considerable blue shift in emission light was consistent going from solution to thin film. These changes particularly in the emission spectra of 4 indicate a reverse effect by the transannular $\pi - \pi$ interaction of the cyclophane unit on optical property of the polymer backbone going from 3a to 4 compared to their respective reference polymers. The above observation suggests that while the transannular effect consistently leads to a significant shift in the emission λ_{max} , it also serves as a novel tuning parameter for the color of the emission light in copolymer 2 with different aromatic chromophores. Apart from the effect of transannular $\pi - \pi$ interaction, steric interaction resulted from the octyl groups in 4 and 16 is also



Figure 4. UV–vis absorption and fluorescence spectra of (a) **5a** and **21** and (b) **6** and **24** measured from solutions (ca. 1×10^{-5} M) in THF at room temperature.

believed to play a role in altering their spectral shifts. Such a steric effect could be easily relieved in **16** by a slight twist of the benzene ring, while in polymer **4**, with the bulkier dithiaparacyclophane, relief of the steric strain is expected to be more difficult. This will result in varied degrees of coplanarity of the thiophene and benzene rings in the polymer backbones of **4** and **16**.

A comparison (Table 2) of the UV-vis absorption and photoluminescence (PL) spectra of polymers 5a and 21 and **6** and **24** in THF (ca. 1×10^{-5} M) is illustrated in Figure 4. Introduction of an acetylene linker and going from **21** to **5a** does not result in any appreciable shift in either the absorption or emission λ_{max} of **5a** (Figure 4a), both emitting blue-green light. In addition, in contrast to the reported alkoxy-substituted PPE 26,²¹ which exhibited an absorption red shift by as much as 40 nm going from solution to thin film, there was only a relatively small red shift observed for **5a** (Table 2). Changing the linker to an ethylene unit and going from the PPV-type copolymer **24** to the cyclophane-based polymer 6 displayed appreciable red shifts (ca. 10 nm, Figure 4b) in both emission and electronic spectra. The emission spectral profile of 6, however, differs significantly from 24 in that the former shows a more intense shoulder at about 449 nm while 24 has a weaker but more apparent shoulder close to 480 nm. The copolymer 6 like 5a exhibits only a small absorption shift (Table 2) going from solution to solid film.





Figure 5. Fluorescence spectra of polymers 5a-c measured from solutions (ca. 1×10^{-5} M) in THF at room temperature.

The effect of transannular $\pi - \pi$ interaction on the optical properties of the copolymers 3a and 4-6 is evidently dependent on the presence or absence and the nature of the "linker" between the cyclophane and the aromatic chromophore. In the absence of a linker, the through-space $\pi - \pi$ interaction of the two parallelstacked benzene rings of the dithiaparacyclophane in the PPP-type copolymers **3a** and **4** results effectively in significant absorption and emission shifts. The PPVtype copolymer 6 shows relatively smaller shifts compared to those in 3a and 4, and in contrast, the PPEtype copolymer 5a (as well as 5b and 5c; refer to later discussion) exhibits negligible shifts relative to the reference polymer **21**. An apparent correlation is that between the transannular effect and the effective conjugation in these copolymers. The polyaryl nature in the polymer backbone of 3a and 4 will provide, due to steric reasons, higher backbone flexibility to coplanarity of the polymer chain. The backbone conjugation may thus be more sensitive to changes in electronic effect induced by the transannular $\pi - \pi$ interaction. On the contrary, the linear acetylene linker in 5 introduces higher backbone rigidity to coplanarity, thus maximizing the conjugation effect in the polymer backbone but minimizing the impact of the transannular $\pi - \pi$ interaction, resulting in very similar absorption and emission spectra of 5a and 21. Earlier reports²² indicate that an ethylene linker allows better electron delocalization than an acetylene unit in some polymers. The ethylene linker, however, also allows more conformational flexibility to the polymer backbone, thus moderating the transannular effect to an intermediate impact.

The above argument, particularly that related to **5a**, could be further supported by comparing the optical properties of the two series of polymers **3a**–**c**¹³ and **5a**–**c**. Both the dimethoxy- and dicyanobenzene units in **3b** ($\phi_{\rm F} = 0.36$) and **3c** ($\phi_{\rm F} = 0$) were found to behave as quenchers (electron acceptors), resulting in significant decreases in PL efficiency compared to that of **3a** ($\phi_{\rm F} = 0.75$). Although the PL efficiency for the series **5a**–**c** is in general lower (Table 2), the changes (Figure 5) going from **5a** ($\phi_{\rm F} = 0.22$) to **5b** ($\phi_{\rm F} = 0.16$) to **5c** ($\phi_{\rm F} = 0.15$) are significantly smaller. This is again consistent with a less effective impact of the transannular effect on the optical properties of the polymer backbone in **5a**–**c**.

Conclusion

In summary, a series of dithia[3.3]paracyclophanebased PPP-, PPE-, and PPV-type copolymers 3-6, respectively, were prepared in this work. The transannular $\pi - \pi$ interaction in the cyclophane unit in the PPP-type 3a-c and 4 induces significant shifts in their absorption and emission spectra compared to those of reference polymers. Both copolymers **3a** and **4** emit blue light, but their emission shifts in opposite direction compared to their respective reference polymers, indicating that the transannular effect could be employed as a tuning parameter in this series of copolymers with different aromatic chromophores linked to the cyclophane. Introduction of a linker between the cyclophane and the aromatic chromophore will apparently improve the rigidity in coplanarity in the polymer backbone and enhance its conjugation effect. This decreases the impact of the transannular $\pi - \pi$ effect in copolymer **6** and makes it ineffective in copolymers 5, which exhibit optical properties derived essentially from only its polymer backbone similar to their reference polymer **21**.

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