Synthesis of Benzo[1,2-*b*:4,3-*b*′]dithiophene/triphenylamine Copolymers: Effects of Substituents on Optical and EL Properties

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Benzo[1,2-*b*:4,3-*b*′]dithiophene/triphenylamine copolymers P-2eh (with no methyl substituents) and P-Me and P-2Me (with methyl substituents at triphenylamine sites) were synthesized by Stille coupling reactions. In the ground state, the methyl substituents at the ortho positions to the BDT unit on the triphenylamine (TPA) moiety in P-Me and P-2Me caused twisting of the polymer structure and clearly limited conjugation of the polymer backbones. However, in their excited states, all of these copolymers were shown to have planar structures, and almost the same emission maxima were observed. This result indicates that, in the excited states, π-conjugation of the polymer backbone results in the adoption of a more stable planar structure rather than the twisted structure observed in the ground state. The maximum EL efficiencies of devices based on P-Me and P-2Me were about three times higher than that of P-2eh due to restricted π-stacking/aggregation of the conjugated copolymers in the solid state and improvements in thermal and electrochemical stability.

Since Tang and VanSlyke reported the first practical multi-layered organic light-emitting diodes (OLEDs),[1] various types of organic material for OLEDs have been developed.[2] In 1990, the Cambridge group reported the preparation of polymer (poly(phenylenevinylene), PPV)-based organic light-emitting diodes (PLEDs),[3] which have attracted much scientific and technological research interest during the past decade due to their simplicity and low-cost fabrication using wet processes, such as inkjet printing as well as their possible application in flexible displays.[4] The main advantages of electroluminescent (EL) conjugated polymers over inorganic and organic small-molecule-based materials in OLEDs are easy processability, ease of formation of large-area thin films, and simple molecular structure design.[5–7] Although many polymers have been investigated for application in PLEDs, further improvements in efficiency, color purity, and durability are still necessary in order to allow development to proceed to the commercial stage for application in full-color flat-panel displays and solid-state lighting. Therefore, detailed investigation of structure–property relationships in EL polymers is required.

We previously reported the fabrication and EL properties of OLEDs using 1,2-diarylethylene derived from the ortho fused heterocyclic compound benzo[1,2-*b*:4,3-*b*′]dithiophene (BDT).[8] This device was shown to give strong emissions (25000 cd m^{-2}), with Commission International de l'Eclairage (CIE) chromaticity coordinates at (0.19, 0.27), in the greenish-blue region. However, this kind of material cannot be used as a single material for an emission layer due to quenching arising from its high planarity and π–π stacking in solid thin films. We also found that 4,5-diphenyl BDT, which contains phenyl groups on the benzene ring, has a non-planar structure due to the torsion angle between BDT and the phenyl groups.

We report herein the synthesis and structure–property relationships of benzo[1,2-*b*:4,3-*b*′]dithiophene/triphenylamine copolymers. Triphenylamine (TPA) derivatives have high hole-transporting abilities[9–17] and large volumes arising from their pyramidal structures.[17–21] Therefore, copolymers with combinations of BDT and TPA moieties are expected to show suppression of inter- or intramolecular interactions due to the non-planar structure of the strained phenyl groups on the benzene ring of BDT and the bulkiness of TPA. The purpose of this study was to investigate the substitution effect on the optical, electrochemical, and EL properties of these materials by synthesis of copolymers containing methyl groups on a polymer backbone.

Results and Discussion

Synthesis and Characterization.   The syntheses of the monomers and corresponding polymers are outlined in Schemes 1–4. Monobromination of triphenylamine (**1**) with *N*-bromosuccinimide (NBS)[22] and subsequent alkylation by the appropriate Grignard reagent in the presence of a Ni^{II} catalyst gave **3**.[23] Monomer **4** was obtained by dibromination of **3** with NBS; the overall yield from the starting material **1** was 31%. We attempted to synthesize the dimethyl monomer **7** from 4-hexylaniline (**5**) by palladium-catalyzed amination using 5 equivalents of 2,5-dibromotoluene (**6**),[24] but an isomeric mixture of **7** and **8** was obtained (47% yield) from which the desired compound **7** could not be isolated. Tetramethyl monomer **11** (19% overall final yield) was also prepared by an amination reaction under similar conditions to the synthesis of **7**, but a 2-step reaction was necessary due to the poor reactivity of sterically hindered bromide **9**. The 2-ethylhexyl group was attached to monomer **4** in order to suppress intermolecular interactions, because it had no methyl substituents which could strain the polymer backbones. 4,5-Diphenylbenzo[1,2-*b*:4,3-*b*′]dithiophene (**14**) was prepared by McMurry coupling of 2-benzoylthiophene (**12**) followed

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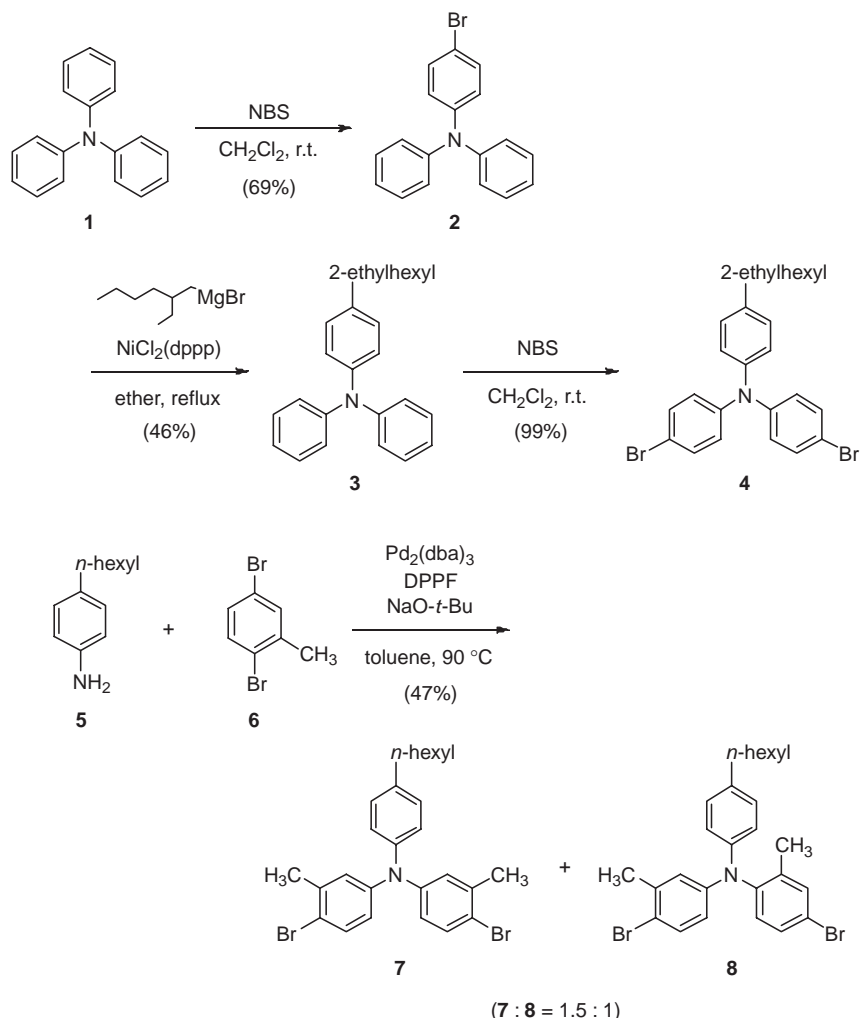
Scheme 1. Synthesis of precursors for coupling reactions.

by photocyclization.[25] Lithiation of **14** using butyllithium and subsequent treatment with excess tributylstannyl chloride gave the distannyl derivative **15**. As shown in Scheme 4, all copolymers (P-2eh, P-Me, and P-2Me) were synthesized by Stille coupling reactions[26] between distannyl compound **15** and the appropriate dibromide (**4**, **7/8**, and **11**, respectively), with a molar ratio of 1.0:1.0.

The resulting polymers were quite soluble in common organic solvents such as chloroform and toluene at room temperature. Table 1 summarizes their molecular weights and thermal properties. The TGA curves of the polymers revealed relatively high thermal stabilities. The 5% weight loss temperatures (T_d) of P-2eh, P-Me, and P-2Me were found to be 418, 474, and 483 °C, respectively. DSC curves showed the glass-transition temperatures (T_g) of P-Me and P-2Me to be 203 and 259 °C. These values were much higher than those of polyfluorene derivatives, which are often used as EL materials (e.g., the T_g of poly(2-(4′-(diphenylamino)phenylenevinyl)-1,4-phenylene-*alt*-9,9-*n*-dihexyl fluorene-2,7-diyl) (PDPF) is reported to be about 159 °C[17]). Although the thermal stability is enhanced as the number of methyl groups on the triphenylamine moiety increases, the different substituents (*n*-hexyl or 2-ethylhexyl group on the phenyl group) and the non-uniform structure of P-Me may also have an influence on thermal sta-

Table 1. Molecular Weights and Thermal Properties of P-2eh, P-Me, and P-2Me

Copolymer	M_n[a]	M_w[a]	D[a]	T_g[b]/°C	T_d[c]/°C
P-2eh	6.5×10^3	1.0×10^4	1.5	—	418
P-Me	3.1×10^3	4.3×10^3	1.3	203	474
P-2Me	4.9×10^3	7.3×10^3	1.5	259	483

a) Molecular weight and polydispersity index (D) were determined by GPC in THF on the basis of polystyrene standards. b) Glass-transition temperature was measured by DSC under N_2. c) 5% weight loss temperature was measured by TGA under N_2.

bility. High thermal stability of the polymers is important from the point of view of PLED performance, as this results in a reduction in morphological changes, deformation, and degradation of the emitting compounds by current-induced heat during the operation of EL devices.[27]
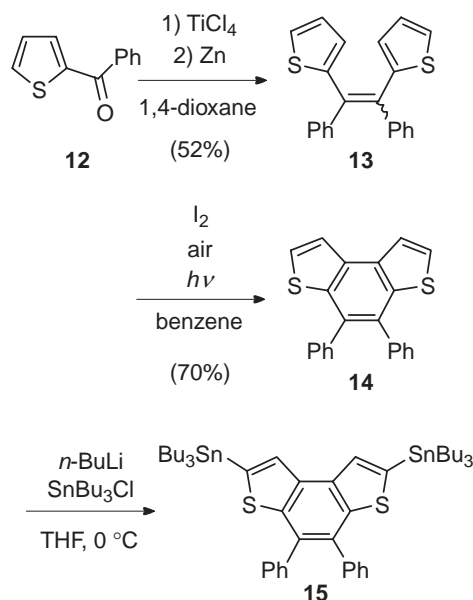
Optical and Photoluminescence Properties. The photophysical properties of P-2eh, P-Me, and P-2Me were determined by UV–vis and fluorescence spectroscopy in toluene solution and in thin films, and the resulting spectra are shown in Figure 1. All polymers had identical absorption spectra in both toluene and thin film, with P-2eh, P-Me, and P-2Me
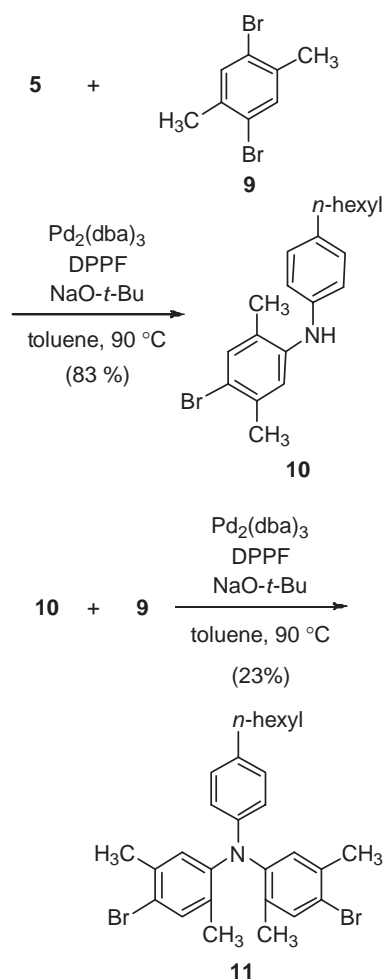
Scheme 2. Synthesis of precursor **11** for coupling reactions.

Scheme 3. Synthesis of precursor **15** for coupling reactions.

Table 2. Absorption Maxima ($\lambda_{\mathrm{max,abs}}$/nm) and Fluorescence Maxima ($\lambda_{\mathrm{max,em}}$/nm) of P-2eh, P-Me, and P-2Me

Copolymer	Solution[a]		Film[c]	
	$\lambda_{\mathrm{max,abs}}$	$\lambda_{\mathrm{max,em}}$[b]	$\lambda_{\mathrm{max,abs}}$	$\lambda_{\mathrm{max,em}}$[b]
P-2eh	405	460	406	505
P-Me	374	464	373	506
P-2Me	360	461	359	508

a) Measured in toluene. b) Excited at the absorption maximum. c) Measured for deposited thin film.

showing maxima at about 405, 374, and 360 nm, respectively, which corresponds to π–π^* transitions. P-Me and P-2Me, which contained methyl substituents at the TPA site, exhibited distinct blue-shifts in their absorption maxima in comparison with the unsubstituted P-2eh. Molecular structure calculations of model compounds using WinMOPAC (Figure 2) suggest that the presence of methyl substituents at ortho positions to the BDT unit on the triphenylamine moiety limits conjugation of the polymer backbones (Table 2).[28]

As shown in Figure 1a, the photoluminescence (PL) spectra of P-2eh, P-Me, and P-2Me in dilute toluene solution were almost the same, with emission maxima at about 460, 464, and 461 nm, respectively. These results can be explained by the stability of the excited states of the copolymers, which is confirmed by the calculations shown in Figure 2. The PL spectra of P-Me and P-2Me revealed broader emissions than those of P-2eh because the methyl substituents in the former two copolymers resulted in restricted rotation around the C–C bond between BDT and the phenyl group. Figure 1b shows the thin-film PL spectra. The fluorescence maxima of these copolymers exhibited significant red-shifts of about 45 nm on changing from dilute solution to the solid state. Based on consideration of the calculated structures shown in Figure 2, these red-shifts can be explained by π-stacking/aggregation arising from higher planarity in the excited states.

Thus, compared with BDT oligomers, the introduction of triphenylamine moieties can result in partial suppression of π-stacking/aggregation of conjugated copolymers in the solid state.[29] The PL spectra of all of the copolymers overlap fully, which suggests that the emissions from these copolymers are from the same excited states.

Electrochemical Properties.   In order to evaluate the electrochemical stability of the copolymers, cyclic voltammetry measurements were carried out at a scan rate of $100\,\mathrm{mV\,s^{-1}}$ in $\mathrm{CH_2Cl_2}$, using tetrabutylammonium perchlorate as an electrolyte. The cyclic voltammograms of P-2eh, P-Me, and P-2Me are shown in Figure 3, and the electrochemical properties and HOMO–LUMO energy gaps (E_{g}) of the copolymers are summarized in Table 3. The HOMO–LUMO energy gaps were determined from the absorption edges for solutions of P-2eh, P-Me, and P-2Me. Although P-Me and P-2Me exhibited reversible oxidation waves, P-2eh showed an irreversible oxidation process. This result indicates that the oxidation potential ($E_{1/2}^{\mathrm{ox}}$) increases in conjunction with the number of methyl substituents on the triphenylamine site. From the cyclic voltammetry measurements (10 cycles), all copolymers, with or without methyl substituents, were shown to have electrochemical stability. The HOMOs of P-2eh, P-Me, and P-2Me were estimated to be -4.98, -5.18, and $-5.22\,\mathrm{eV}$, respectively. These values are close to those of the HOMO of PEDOT/
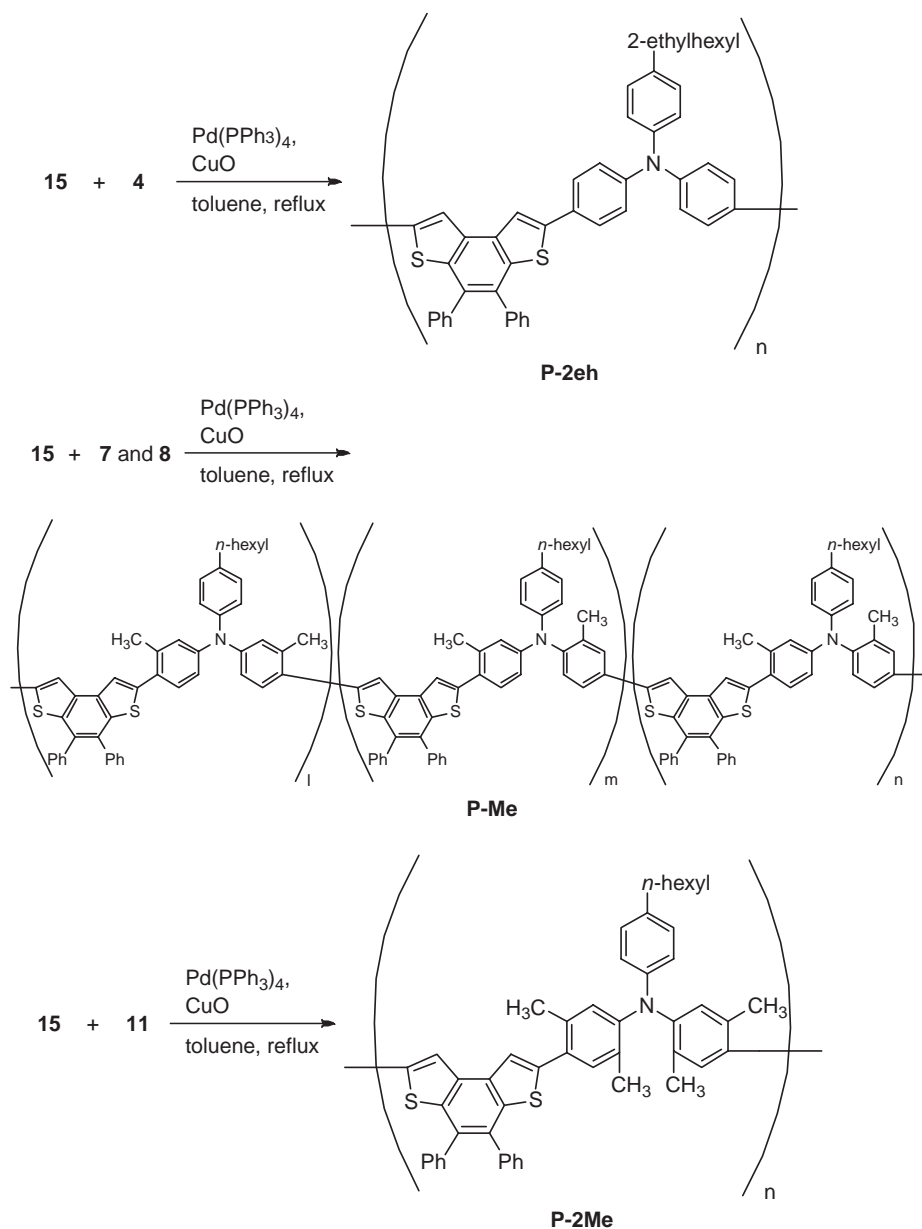
Scheme 4. Synthesis of P-2eh, P-Me, and P-2Me.

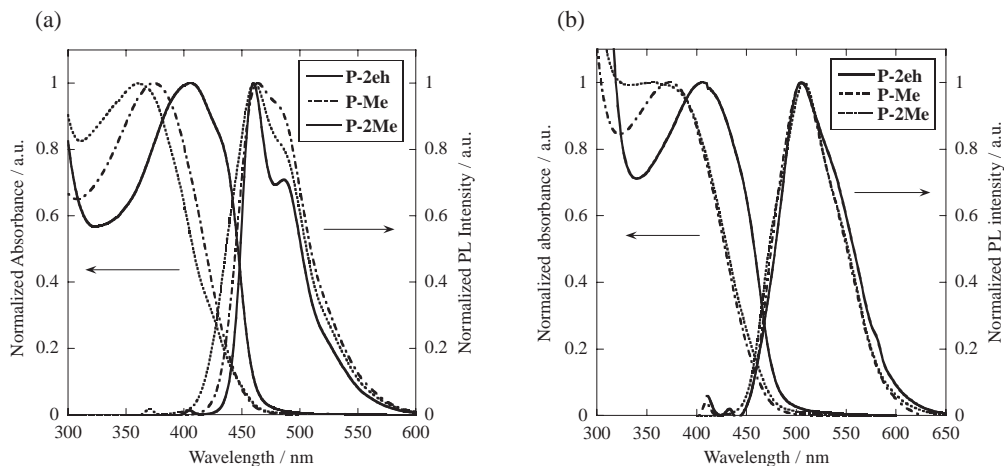**Figure 1.** Absorption and photoluminescence spectra of P-2eh, P-Me, and P-2Me (a) in dilute toluene solution; (b) in thin films.

Model Compounds

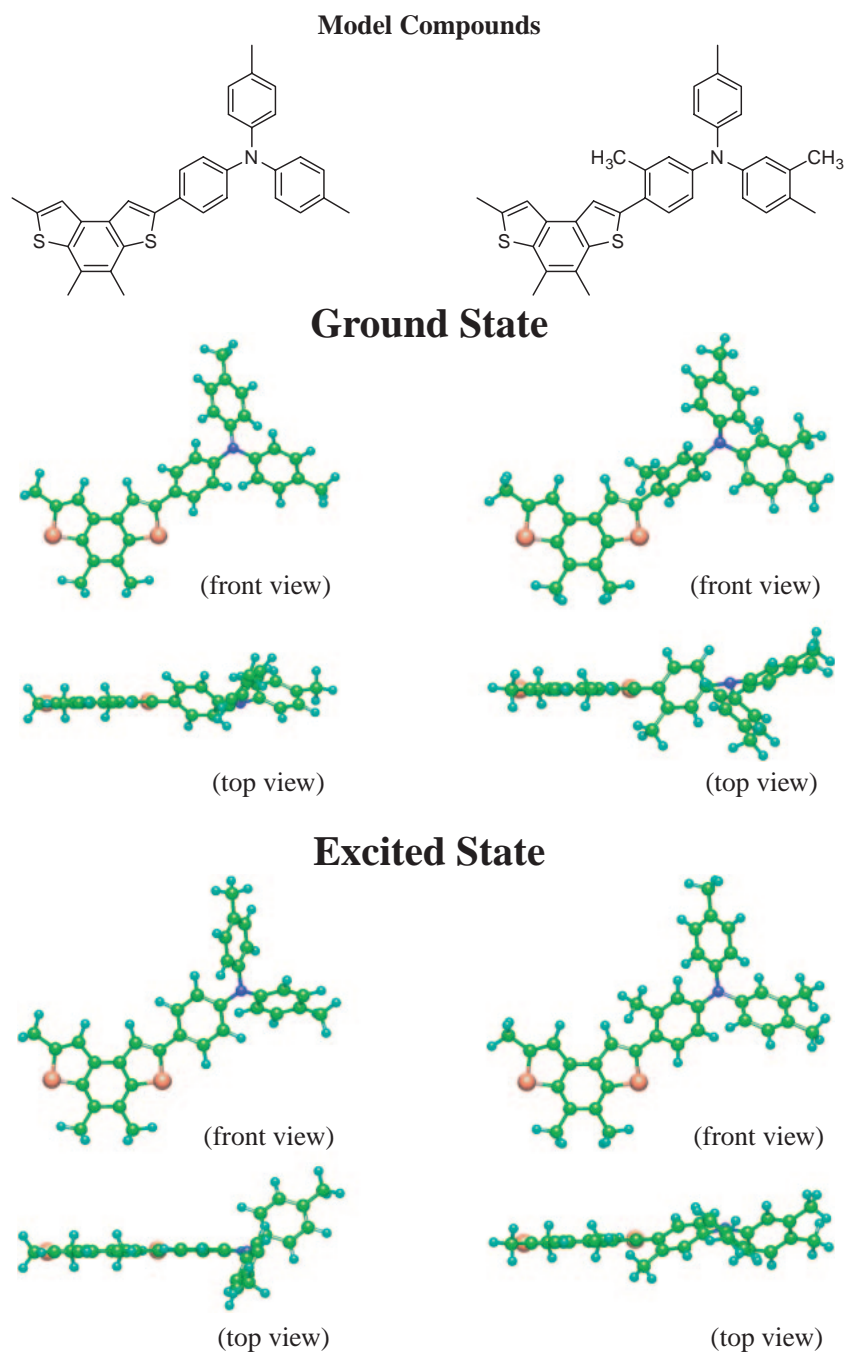**Ground State**

Excited State

Figure 2. Molecular structures of model compounds calculated by WinMOPAC (PM5).

PSS (-5.0 eV), and thus hole injection from PEDOT/PSS to these copolymers is expected to be comparatively easy.[17]

Electroluminescence Properties. Double-layer OLED devices (type A) with the configuration ITO/PEDOT:PSS (40 nm)/copolymer (35 nm)/Ca (30 nm)/Al (100 nm) were fabricated using P-2eh, P-Me, and P-2Me (devices I–III, respectively). The emission layer was fabricated by spin-coating from toluene solution (1.0 wt %). The EL spectrum of each copolymer exhibited a similar emission to the corresponding thin-film PL spectrum. The characteristics of the OLEDs are summarized in Table 4. As shown in Figure 4, the turn-on voltages of the OLEDs based on P-2eh, P-Me, and P-2Me were 7.0, 4.5, and 6.0 V, respectively, which are similar to those

of analogous double-layer OLED devices, such as PDPF (5.0 V).[17] The maximum luminances of devices I–III were 213 (at 12.0 V), 1054 (at 8.5 V), and 936 cd m^{-2} (at 10.5 V), and their maximum EL efficiencies were 0.025, 0.078, and 0.071 cd A^{-1}, respectively. The maximum EL efficiencies of the devices based on P-Me and P-2Me, which contain methyl substituents, were about 3 times higher than that of P-2eh, which contains no methyl substituent. This difference is thought to be due to restriction of π-stacking/aggregation in the solid state and a resulting improvement in thermal and electrochemical stability.

The EL performances of type A devices I–III were poor, probably due to a lack of electron-transporting ability. The in-
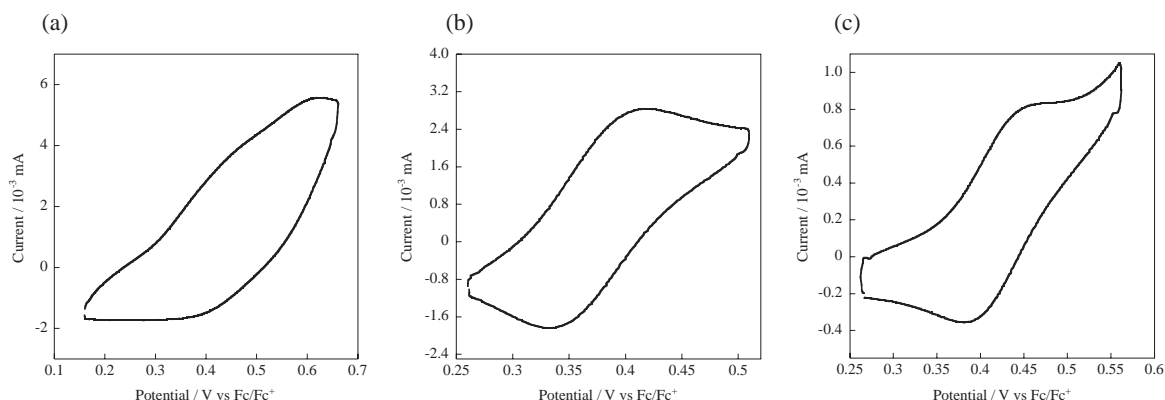
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Figure 3. CV curves (10 cycles) of (a) P-2eh, (b) P-Me, and (c) P-2Me at a scan rate of $100 \, mV \, s^{-1}$ in CH_2Cl_2 (1.0×10^{-4} $mol \, dm^{-3}$) with tetrabutylammonium perchlorate ($0.1 \, mol \, dm^{-3}$).

Table 3. Electrochemical Properties of P-2eh, P-Me, and P-2Me

Copolymer	$E_{1/2}^{ox \, a)}$ vs. $(Fc^+/Fc)/V$	$E_{HOMO}^{b)}$ /eV	$E_{LUMO}^{c)}$ /eV	$E_g^{d)}$ /eV
P-2eh	$0.18^{e)}$	−4.98	−2.30	2.68
P-Me	0.38	−5.18	−2.51	2.67
P-2Me	0.42	−5.22	−2.58	2.64

a) $E_{1/2}^{ox}$ potentials (vs. Fc/Fc^+ couple) were determined by cyclic voltammetry in CH_2Cl_2 ($1.0 \times 10^{-4} \, mol \, dm^{-3}$) containing tetrabutylammonium perchlorate ($0.1 \, mol \, dm^{-3}$) as a supporting electrolyte. b) E_{HOMO} was estimated from $E_{1/2}^{ox}$ using Fe/Fe^+ couple ($E_{1/2}^{ox} = 0.54$) as an internal standard. $E_{HOMO} = -4.8 - E_{1/2}^{ox}$. c) E_{LUMO} was calculated approximately by subtracting E_g from E_{HOMO}. d) E_g was determined from the optical absorption edge in toluene solution. $E_g = 1240/$ (wavelength of the absorption edge) (eV). e) E_{onset}^{ox} potential vs. Fc/Fc^+ couple ($E_{onset}^{ox} = 0.44$).

troduction of a triphenylamine moiety enhanced only hole-transporting ability, and the balance of hole and electron injection/transport was poor. Therefore, we replaced the emission layer of the OLED with P-Me containing 10% 2-(4-biphenyl-yl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD,[2b] used as an electron-transporting material), which was fabricated by spin-coating from toluene solution (1.0 wt %). The structure of the resulting double-layer OLED (device IV) was ITO/PEDOT: PSS (40 nm)/P-Me:PBD (9:1) (35 nm)/Ca (30 nm)/Al (100 nm). The characteristics of this OLED are shown in Table 4. The maximum luminance was $1848 \, cd \, m^{-2}$ (at 8.0 V), and the maximum EL efficiency was $0.14 \, cd \, A^{-1}$, which was about

twice as high as that of device II (containing P-Me only). This difference is probably due to improvement of the carrier balance by enhancement of electron-transporting ability.[2b]

While the addition of an electron-transporting material leads to enhancement of EL efficiency, it is still probable that in devices I–IV, the injected holes and electrons (mainly the holes) partially pass through without recombination at the emitting layer.[31] Therefore, a type B multi-layer OLED device with the configuration ITO/PEDOT:PSS (40 nm)/P-Me (35 nm)/ BCP (30 nm)/Alq$_3$ (30 nm)/LiF (0.5 nm)/Al (100 nm) was fabricated (device V). The characteristics of this type B OLED are shown in Table 4. As expected, the introduction of the hole-blocking BCP layer and the electron-transporting Alq$_3$ layer resulted in improved EL performance. The EL efficiency of device V was 5 times higher than that of device IV. These results indicate that the EL efficiency of type B devices is enhanced by suppression of the carrier passage due to the introduction of a hole-blocking BCP layer and by improvement of the carrier balance due to the introduction of an electron-transporting Alq$_3$ layer.

Summary

Benzodithiophene/triphenylamine copolymers P-2eh (with no methyl substituent) and P-Me and P-2Me (containing methyl substituents at triphenylamine sites) were synthesized by Stille coupling reactions. The thermal stability was enhanced as the number of methyl groups on the triphenylamine moiety increased. The absorption spectra in toluene solution and in thin film suggests that the presence of methyl substituents at ortho positions to the BDT unit on the triphenylamine moiety limits conjugation in the polymer backbone, leading to

Table 4. Electroluminescence Properties of Type A and Type B Devices

Device	Copolymer	EL λ_{max} /nm	$V_{on}^{a)}$ /V	$L_{max}^{b)}$ /cd m^{-2}	Efficiency$^{c)}$ /cd A^{-1}	$\eta_{ex}^{d)}$ /%
I (Type A)	P-2eh	505	7.0	213 (at 12.0 V)	0.025 (at 9.0 V)	0.081
II (Type A)	P-Me	500	4.5	1054 (at 8.5 V)	0.078 (at 8.5 V)	0.027
III (Type A)	P-2Me	500	6.0	936 (at 10.5 V)	0.071 (at 10.0 V)	0.025
IV (Type A)	P-Me:PBD (9:1)	500	5.5	1848 (at 8.0 V)	0.14 (at 8.0 V)	0.047
V (Type B)	P-Me	515	7.5	1861 (at 17.0 V)	0.71 (at 11.0 V)	0.20

a) Turn-on voltage: the voltage required for a device to reach a luminance of about $1 \, cd \, m^{-1}$. b) Luminance at maximum bias voltage. c) Maximum EL efficiency. d) Maximum external quantum efficiency.[30]
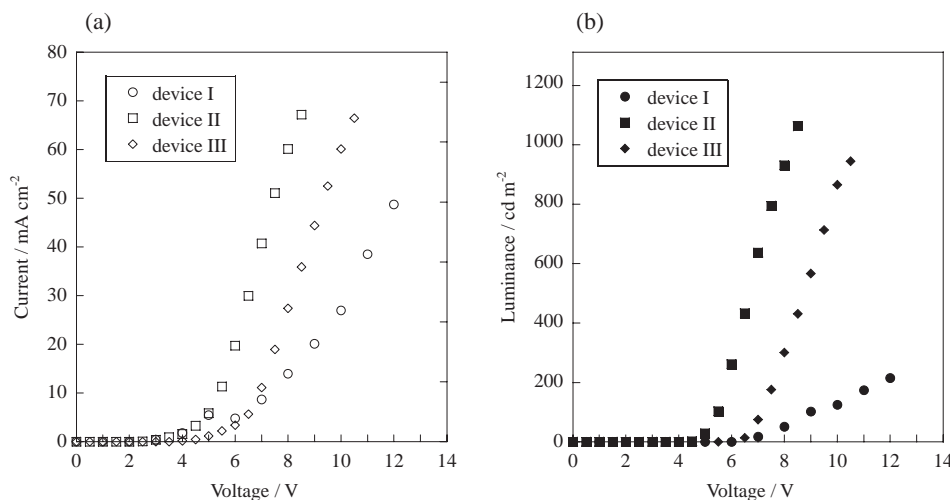
Figure 4.   (a) Current density–voltage and (b) luminance–voltage characteristics of devices I–III.

a blue shift in the absorption maximum. The PL spectra of all three copolymers in toluene solution and in thin film overlapped fully, which indicated that the emissions from these copolymers were from the same excited states. Although P-Me and P-2Me exhibited reversible oxidation waves in cyclic voltammetry measurements, P-2eh showed an irreversible oxidation process. The maximum EL efficiencies of devices based on P-Me and P-2Me were about 3 times higher than that of P-2eh, because the presence of methyl substituents resulted in restriction of π-stacking/aggregation of the conjugated copolymers in the solid state and improvement of the thermal and electrochemical stability.

Experimental

All reactions were carried out under an atmosphere of argon unless otherwise noted. Anhydrous THF was purchased from Kanto Chemical Co. and used without further purification. Dichloromethane was distilled from calcium hydride and stored over 4 Å molecular sieves. Toluene was distilled from sodium and stored over 4 Å molecular sieves. A hexane solution of butyllithium (Kanto Chemical Co.) was titrated using diphenylacetic acid. Melting points were determined using a Yanako MP-S3 hot stage apparatus and were not corrected. Thin layer chromatography was performed using Merck precoated silica gel sheets 60 F_{254}. Silica gel (Fuji Silysia PSQ100B) was used for column chromatography. NMR spectra were obtained using a JNM-AL 300 FT NMR (300 MHz) or JNM-ECA 400 FT NMR (400 MHz) spectrometer in CDCl$_3$ solution with tetramethylsilane as an internal standard. The molecular weights and polydispersity indices of the copolymers were determined by gel permeation chromatography (GPC) analysis relative to a polystyrene standard using GPC columns (TSKgel MultiporeH$_{XL}$-M, TOSOH) using THF as an eluent at 40 °C. The 5% weight loss temperatures were determined using a TG/DTA6200 instrument (SII NanoTechnology), and the glass-transition temperatures were determined using a DSC6200 instrument (SII NanoTechnology). IR spectra were recorded on a FT/IR-420 Fourier transform infrared spectrometer (JASCO). Elemental analysis was performed using a JM10 Micro Corder (J-Science Lab). UV spectra were recorded on a V-530 instrument (JASCO). Photoluminescence spectra were recorded on a FP-6200 instrument (JASCO). Cyclic voltammograms were recorded using

a HSV-100 instrument (Hokuto Denko) in dichloromethane containing n-Bu$_4$N$^+$ClO$_4^-$ (0.1 mol dm^{-3}) as a supporting electrolyte at a scan rate of 100 mV s^{-1}. The counter and working electrodes were made from Pt, and the reference electrode was Ag/AgCl.

The organic layers of the EL devices were prepared by spin coating from toluene. The devices were tested in air under ambient conditions with no encapsulation. EL spectra, device luminances, and current–voltage characteristics were recorded by combining a BM-9 luminance meter (Topcon) and a Photal MCPD-7000 (Otsuka Electronics).

4-Bromotriphenylamine (2).   To a stirred solution of triphenylamine (5.00 g, 20.4 mmol) in dry CH$_2$Cl$_2$ (80 mL) was added NBS (3.63 g, 20.4 mmol) and the mixture was stirred at room temperature for 2 h. Aqueous Na$_2$S$_2$O$_3$ and NaHCO$_3$ were then added and the organic layer was separated. The crude product was purified by silica gel column chromatography (hexane), and the resulting material was recrystallized from ethanol to give **2** (4.59 g, 69%) as a white solid. Mp 115–116 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.94 (2H, d, $J = 8.7$ Hz), 7.03 (2H, t, $J = 7.5$ Hz), 7.06 (4H, d, $J = 7.8$ Hz), 7.25 (4H, dt, $J = 1.5, 7.8$ Hz), 7.31 (2H, d, $J = 8.7$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ 114.7, 123.2, 124.4, 125.1, 129.3, 132.1, 147.4; IR (KBr) 1486, 1334, 1284, 1073, 1003, 824 cm^{-1}; Anal. Found: C, 66.48; H, 4.56; N, 4.31%. Calcd for C$_{18}$H$_{14}$BrN: C, 66.68; H, 4.35; N, 4.32%.

4-(2-Ethylhexyl)triphenylamine (3).   To a stirred solution of **2** (3.00 g, 9.25 mmol) and NiCl$_2$(dppp) (0.10 g, 0.19 mmol) in ether (70 mL) was added a stirred suspension of 2-ethylhexylmagnesium bromide [9.25 mmol, prepared from Mg (0.47 g, 19.4 mmol) and 1-bromo-2-ethylhexane (3.29 mL, 0.19 mmol) in 30 mL of ether] at 0 °C. The reaction mixture was allowed to warm to room temperature over 1.5 h, followed by refluxing for 3 h. The crude product was purified by silica gel column chromatography (hexane) to give **3** (1.52 g, 46%) as a colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.88 (6H, t, $J = 7.3$ Hz), 1.25–1.35 (9H, m), 2.48 (2H, d, $J = 6.9$ Hz), 6.96 (2H, d, $J = 7.3$ Hz), 7.01 (2H, t, $J = 6.9$ Hz), 7.06 (4H, dd, $J = 1.2, 8.4$ Hz), 7.22 (4H, dt, $J = 1.2, 8.4$ Hz), 7.26 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ 10.8, 14.1, 23.1, 25.5, 28.9, 32.3, 39.5, 41.1, 122.2, 123.7, 124.5, 129.1, 129.9, 136.7, 145.3, 148.1; IR (Si) 3031, 2923, 2861, 1589, 1496, 1280, 836, 752, 698 cm^{-1}; Anal. Found: C, 87.51; H, 8.78; N, 4.07%. Calcd for C$_{26}$H$_{31}$N: C, 87.34; H, 8.74; N, 3.92%.

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4,4′-Dibromo-4″-(2-ethylhexyl)triphenylamine (4). To a stirred solution of **3** (0.33 g, 0.93 mmol) in dry CH_2Cl_2 (20 mL) was added NBS (0.36 g, 2.05 mmol) and the mixture was stirred at room temperature for 3 h. The crude product was purified by silica gel column chromatography (hexane) to give **4** (0.47 g, 99%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (6H, t, $J = 7.2$ Hz), 1.25–1.35 (9H, m), 2.48 (2H, d, $J = 6.9$ Hz), 6.90 (4H, d, $J = 9.0$ Hz), 6.95 (2H, d, $J = 8.7$ Hz), 7.04 (2H, d, $J = 8.7$ Hz), 7.30 (4H, d, $J = 9.0$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.8, 14.1, 23.0, 25.5, 28.8, 32.3, 39.5, 41.0, 114.9, 124.8, 125.0, 130.3, 132.2, 137.9, 144.3, 146.7; IR (Si) 2959, 2925, 2857, 1485, 1310, 1284, 1071, 1007, 820 cm^{-1}; Anal. Found: C, 60.77; H, 5.95; N, 2.60%. Calcd for $C_{26}H_{29}Br_2N$: C, 60.60; H, 5.67; N, 2.72%.

Triarylamine Mixture 7 and 8. To a stirred solution of $Pd_2(dba)_3$ (54.9 mg, 0.06 mmol) and DPPF (55.5 mg, 0.10 mmol) in toluene (6 mL) was added 2,5-dibromotoluene (0.58 mL, 4.20 mmol) at room temperature, and the resulting mixture was stirred for 10 min. NaO-*t*-Bu (0.48 g, 5.00 mmol) and 4-hexylaniline (0.39 mL, 2.0 mmol) were then added to the solution and the mixture was stirred at 90 °C for 24 h. The crude product was purified by alumina column chromatography (40:1 hexane–ethyl acetate) to give **7** and **8** (0.48 g, 47%, 1.5:1 from ^1H NMR) as a colorless oil. IR (Si) 3023, 2923, 2857, 1589, 1477, 1311, 1261, 1025, 813 cm^{-1}; Anal. Found: C, 60.51; H, 5.91; N, 2.75%. Calcd for $C_{26}H_{29}Br_2N$: C, 60.60; H, 5.67; N, 2.72%.

N-(4-Bromo-2,5-dimethylphenyl)-4-hexylaniline (10). To a stirred solution of $Pd_2(dba)_3$ (65 mg, 0.07 mmol) and DPPF (66 mg, 0.12 mmol) in toluene (8 mL) was added 2,5-dibromo-*p*-xylene (1.5 g, 5.7 mmol) at room temperature, and the resulting mixture was stirred for 10 min. NaO-*t*-Bu (0.57 g, 5.9 mmol) and 4-hexylaniline (0.46 mL, 2.4 mmol) were then added to the solution and the mixture was stirred at 90 °C for 24 h. The crude product was purified by silica gel column chromatography (20:1, hexane–ethyl acetate) to give **10** (0.71 g, 83%) as a wine-red oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, $J = 6.9$ Hz), 1.26–1.37 (6H, m), 1.55–1.64 (2H, m), 2.18 (3H, s), 2.28 (3H, s), 2.55 (2H, t, $J = 7.9$ Hz), 5.21 (1H, s), 6.90 (2H, d, $J = 8.4$ Hz), 7.03 (1H, s), 7.09 (2H, d, $J = 8.4$ Hz), 7.30 (1H, s); IR (Si) 2926, 2855, 1607, 1562, 1515, 1389, 1312, 1265, 971 cm^{-1}.

N,N-Bis(4-bromo-2,5-dimethylphenyl)-4-hexylaniline (11). To a stirred solution of $Pd_2(dba)_3$ (54 mg, 0.06 mmol) and DPPF (55 mg, 0.10 mmol) in toluene (5 mL) was added 2,5-dibromo-*p*-xylene (2.1 g, 7.9 mmol) at room temperature, and the resulting mixture was stirred for 10 min. NaO-*t*-Bu (0.38 g, 3.9 mmol) and **10** (0.71 g, 2.0 mmol) were then added to the solution and the mixture was stirred at 90 °C for 3 days. The crude product was purified by silica gel column chromatography (hexane) to give **11** (0.25 g, 23%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 0.85–0.90 (3H, m), 1.27–1.34 (6H, m), 1.55–1.63 (2H, m), 1.89 (6H, s), 2.25 (6H, s), 2.52 (2H, t, $J = 7.5$ Hz), 6.58 (2H, d, $J = 8.4$ Hz), 6.76 (2H, s), 6.96 (2H, d, $J = 8.4$ Hz), 7.33 (2H, s); IR (Si) 2924, 2856, 1718, 1363, 1222, 977 cm^{-1}.

4,5-Diphenylbenzo[1,2-*b*:4,3-*b*′]dithiophene (14). A stirred solution of **13** (5.00 g, 14.52 mmol) and iodine (0.07 g, 0.28 mmol) in benzene (1600 mL) was irradiated with a high-pressure mercury lamp under air for 12 h at room temperature. The reaction mixture was then washed with aqueous $Na_2S_2O_3$, concentrated, and filtered through a celite pad. The filtrate was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by alumina and silica gel column chromatography (hexane) to give **14** (3.42 g, 70%) as white crystals. Mp 177–178 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.25–7.37 (m, 10H), 7.55 (2H, d, $J = 5.6$ Hz), 7.79 (2H, d, $J = 5.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.1, 127.2, 127.3, 128.1, 130.2, 131.3, 133.65, 139.2, 139.4; IR (KBr) 3056, 1758, 1442, 849, 666 cm^{-1}; Anal. Found: C, 77.10; H, 4.08%. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12%.

4,5-Diphenyl-2,7-bis(tributylstannyl)benzo[1,2-*b*:4,3-*b*′]dithiophene (15). To a stirred solution of **14** (0.20 g, 0.58 mmol) in THF (4 mL) was added butyllithium (1.45 mmol, 0.96 mL of 1.5 mol dm^{-3} hexane solution) at 0 °C, and the mixture was stirred for 1.5 h. To the resulting brown solution was added tributylstannyl chloride (0.44 mL, 1.62 mmol) at 0 °C, and the reaction mixture was stirred for 3 h. The mixture was filtered through a celite pad, the filtrate was concentrated, and the residue was dried in vacuo to give **15** (crude) as light yellow oil. The crude product **15** was used for the subsequent reaction without further purification.

P-2eh. To a stirred solution of dibromide **4** (0.10 g, 0.19 mmol) and stannyl compound **15** (0.26 g, 0.28 mmol) in toluene (3 mL) were added $Pd(PPh_3)_4$ (13.2 mg, 0.0114 mmol) and CuO (33.2 mg, 0.42 mmol), and the mixture was refluxed for 24 h. After cooling, the reaction was filtrated through a celite pad. The crude product was dissolved in a small amount of chloroform and poured into 500 mL of methanol. The resulting precipitate was collected by filtration, washed with methanol, and dried in vacuo to give P-2eh as a yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 0.79–0.92 (6H, m), 1.15–1.38 (9H, m), 2.43–2.55 (2H, m), 7.00–7.14 (8H, m), 7.19–7.38 (14H, m), 7.55–7.64 (1H, m), 7.84–7.92 (1H, m); IR (KBr) 3028, 2923, 1599, 1492, 1321, 1286, 1182, 1119, 699 cm^{-1}; Anal. Found: C, 80.79; H, 6.02; N, 1.82%.

P-Me. To a stirred solution of dibromides **7** and **8** (0.10 g, 0.19 mmol) and stannyl compound **15** (0.26 g, 0.28 mmol) in toluene (2 mL) were added $Pd(PPh_3)_4$ (13.2 mg, 0.0114 mmol) and CuO (33.2 mg, 0.42 mmol), and the mixture was refluxed for 24 h. After cooling, the reaction was filtered through a celite pad. The crude product was dissolved in a small amount of chloroform and poured into 500 mL of methanol. The resulting precipitate was collected by filtration, washed with methanol, and dried in vacuo to give P-Me as a yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 0.86–0.92 (3H, m), 1.24–1.39 (6H, m), 1.58–1.67 (2H, m), 2.08 (1H, s), 2.41–2.46 (5H, m), 2.53–2.62 (2H, m), 6.93–7.12 (6H, m), 7.23–7.40 (14H, m), 7.53–7.81 (2H, m); IR (KBr) 3022, 2923, 1598, 1483, 1320, 1259, 1119, 1031, 698 cm^{-1}; Anal. Found: C, 81.07; H, 5.40; N, 1.13%.

P-2Me. To a stirred solution of dibromide **11** (70 mg, 0.13 mmol) and stannyl compound **15** (0.15 mmol) in toluene (1.5 mL) were added $Pd(PPh_3)_4$ (9.0 mg, 0.0077 mmol) and CuO (23 mg, 0.28 mmol), and the mixture was refluxed for 2 d. After cooling, the reaction was filtrated through a celite pad. The crude product was dissolved in a small amount of chloroform and poured into 500 mL of methanol. The resulting precipitate was collected by filtration, washed with methanol, and dried in vacuo to give P-2Me as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 0.84–0.91 (3H, m), 1.26–1.36 (6H, m), 1.55–1.64 (2H, m), 1.96 (6H, s), 2.41 (6H, s), 2.49–2.57 (2H, m), 6.70 (2H, d, $J = 7.5$ Hz), 6.87 (2H, s), 7.00 (2H, d, $J = 7.5$ Hz), 7.22–7.42 (12H, m), 7.69–7.78 (2H, m); IR (KBr) 3022, 2923, 1601, 1493, 1320, 1119, 699 cm^{-1}; Anal. Found: C, 82.16; H, 5.84; N, 1.36%.

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