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Supporting Information

for

**Tuning the Absorption, Charge Transport Properties and
Solar Cell Efficiency with the Number of Thienyl Rings in
Platinum-containing Poly(aryleneethynylene)s**

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Experimental

Synthesis of 1-bromo-undecan-2-one. Bromine (10.4 g, 65.1 mmol) was added dropwise to a stirred solution of 2-undecanone (11.1 g, 64.9 mmol) in methanol (100 mL) at $-10\text{ }^{\circ}\text{C}$. The mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 1 h and then another 1 h at room temperature. Water (20 mL) and then concentrated sulfuric acid (35 mL) were added to the mixture in an ice bath. After the mixture was stirred overnight at room temperature, white crystals precipitated from the reaction mixture. The precipitate was filtered, washed with water, and then dried to produce 1-bromo-undecan-2-one (15.2 g, 94%). ^1H NMR (CDCl_3): $\delta = 3.87$ (s, 2H, CH_2Br), 2.65–2.61 (t, 2H, $\text{C}_8\text{H}_{17}\text{CH}_2\text{CO}$), 1.61–1.58 (m, 2H, $\text{C}_7\text{H}_{15}\text{CH}_2\text{CH}_2$), 1.32–1.25 (m, 12H, $\text{CH}_3\text{C}_6\text{H}_{12}$ –), 0.88–0.83 ppm (t, 3H, CH_3); ^{13}C NMR (CDCl_3): $\delta = 202.29$ (CO), 39.84, 34.30, 31.82, 29.36, 29.30, 29.22, 29.01, 23.84, 22.64, 14.08 ppm (nonyl + CH_2); FAB-MS: m/z 249 (M^+); Anal. Calcd (%) for $\text{C}_{11}\text{H}_{21}\text{BrO}$: C, 53.02; H, 8.49. Found: C, 52.98; H, 8.33.

Synthesis of 4,4'-Dinonyl-2,2'-bithiazole. 1-Bromo-undecan-2-one (5.23 g, 21.0 mmol), dithiooxamide (1.20 g, 10.0 mmol) and ethanol (50 mL) were placed in a 100 mL, two-necked, round-bottom flask equipped with a reflux condenser. The solution was heated to reflux for 6 h, and after cooling, it was poured onto the crushed ice. The mixture was extracted with dichloromethane and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product was obtained as a pale yellow solid in 89%. Yield (3.74 g) ^1H NMR (CDCl_3): $\delta = 6.93$ (s, 2H, Ar), 2.81–2.77 (t, 4H, nonyl), 1.76–1.68 (m, 4H, nonyl), 1.33–1.25 (m, 24H, nonyl), 0.88–0.85 ppm (t, 6H, nonyl); ^{13}C NMR (CDCl_3): $\delta = 160.84$, 159.16, 114.54 (Ar), 31.87, 31.53, 29.52, 29.42, 29.30, 29.25, 29.18, 22.67, 14.11 ppm (nonyl); FAB-MS: m/z 420 (M^+); Anal. Calcd (%) for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{S}_2$: C, 68.52; H, 9.58; N, 6.66. Found: C, 68.38; H, 9.43; N,

6.48.

Synthesis of 5,5'-Dibromo-4,4'-dinonyl-2,2'-bithiazole (L0-2Br). 4,4'-Dinonyl-2,2'-bithiazole (2.10 g, 5.00 mmol) and NBS (1.80 g, 10.1 mmol) were dissolved in a mixture of acetic acid (30 mL) and *N,N*-dimethylformamide (30 mL). After 4 h of stirring in the dark, a solid precipitated in the reaction mixture. The precipitate was filtered, washed with methanol, and then dried to produce 5,5'-dibromo-4,4'-dinonyl-2,2'-bithiazole as white needles after recrystallization from CH₂Cl₂/hexane (2.69 g, 93%). ¹H NMR (CDCl₃): δ = 2.75–2.71 (t, 4H, nonyl), 1.70–1.60 (m, 4H, nonyl), 1.32–1.26 (m, 24H, nonyl), 0.88–0.85 ppm (t, 6H, nonyl); ¹³C NMR (CDCl₃): δ = 159.91, 157.38, 106.80 (Ar), 31.88, 29.50, 29.47, 29.35, 29.30, 29.12, 28.68, 22.67, 14.11 ppm (nonyl); FAB-MS: *m/z* 578 (M⁺); Anal. Calcd (%) for C₂₄H₃₈N₂Br₂S₂: C, 49.83; H, 6.62; N, 4.84. Found: C, 49.90; H, 6.55; N, 4.77.

Synthesis of 5,5'-Dithienyl-4,4'-dinonyl-2,2'-bithiazole. To a suspension of magnesium (0.78 g, 32.0 mmol) in anhydrous diethyl ether (20 mL), a solution of 2-bromothiophene (5.22 g, 32.0 mmol) in anhydrous diethyl ether (100 mL) was added dropwise. The as-prepared Grignard reagent was then added dropwise to an ice-cooled suspension of 5,5'-dibromo-4,4'-dinonyl-2,2'-bithiazole (4.63 g, 8.00 mmol) and Pd(dppf)Cl₂ (0.20 g) in anhydrous diethyl ether (30 mL). The reaction mixture was stirred for 1 h at room temperature. It was then hydrolyzed with a saturated aqueous ammonium chloride solution, and this was followed by the addition of diethyl ether. The organic layer was washed three times with water (200 mL) and dried over sodium sulfate. After the removal of solvent, recrystallization from dichloromethane and hexane gave the target product as a yellow solid (4.40 g, 94%). ¹H NMR (CDCl₃): δ = 7.37–7.36 (d, 2H, Ar), 7.19–7.18 (d, 2H, Ar), 7.10–7.08 (m, 2H, Ar), 2.94–2.90 (t, 4H, nonyl), 1.81–1.73 (m, 4H, nonyl), 1.39–1.25 (m, 24H, nonyl), 0.88–0.85 ppm (t, 6H, nonyl); ¹³C NMR (CDCl₃): δ = 157.79,

154.54, 132.97, 127.72, 127.46, 127.40, 126.44 (Ar), 31.88, 30.29, 29.53, 29.47, 29.56, 29.41, 29.30, 22.67, 14.11 ppm (nonyl); FAB-MS: m/z 584 (M^+); Anal. Calcd (%) for $C_{32}H_{44}N_2S_4$: C, 65.71; H, 7.58; N, 4.79. Found: C, 65.67; H, 7.43; N, 4.64.

Synthesis of 2,2'-Dibromo-5,5'-dithienyl-4,4'-dinonyl-2,2'-bithiazole (L1-2Br). 5,5'-Dithienyl-4,4'-dinonyl-2,2'-bithiazole (2.34 g, 4.00 mmol) was dissolved in a mixture of chloroform (50 mL) and acetic acid (10 mL). NBS (1.50 g, 8.42 mmol) was then added to the solution which was then stirred for 1 h in the dark. The precipitate in the reaction mixture was filtered, washed with methanol, and dried to produce a yellow solid with a yield of 97% (2.88 g). 1H NMR ($CDCl_3$): δ = 7.04–7.03 (d, 2H, Ar), 6.93–6.92 (d, 2H, Ar), 2.88–2.85 (t, 4H, nonyl), 1.78–1.71 (m, 4H, nonyl), 1.38–1.25 (m, 24H, nonyl), 0.88–0.85 ppm (t, 6H, nonyl); ^{13}C NMR ($CDCl_3$): δ = 157.98, 155.05, 134.36, 130.54, 127.68, 126.65, 113.27 (Ar), 31.88, 30.25, 29.51, 29.44, 29.40, 29.38, 29.30, 22.68, 14.12 ppm (nonyl); FAB-MS: m/z 742 (M^+); Anal. Calcd (%) for $C_{32}H_{42}N_2Br_2S_4$: C, 51.75; H, 5.70; N, 3.77. Found: C, 51.62; H, 5.75; N, 3.67.

Synthesis of 5,5'-Bis(bithienyl)-4,4'-dinonyl-2,2'-bithiazole. To a suspension of magnesium (0.40 g, 16.0 mmol) in anhydrous diethyl ether (20 mL), a solution of 2-bromothiophene (2.60 g, 16.0 mmol) in anhydrous diethyl ether (80 mL) was added dropwise. The Grignard reagent prepared was then added dropwise to an ice-cooled suspension of **L1-2Br** (2.97 g, 4.00 mmol) and $Pd(dppf)Cl_2$ (100 mg) in anhydrous diethyl ether (30 mL). The reaction mixture was stirred for 2 h at room temperature. It was then hydrolyzed with a saturated aqueous ammonium chloride solution, and this was followed by the addition of diethyl ether. The red layer was washed three times with water (200 mL) and dried over sodium sulfate. After the removal of solvent, recrystallization from dichloromethane and hexane gave

the brown product (2.58 g, 86%). ^1H NMR (CDCl_3): δ = 7.27–7.24 (m, 2H, Ar), 7.21–7.20 (m, 2H, Ar), 7.14–7.13 (d, 2H, Ar), 7.09–7.08 (d, 2H, Ar), 7.05–7.02 (m, 2H, Ar), 2.97–2.93 (t, 4H, nonyl), 1.83–1.75 (m, 4H, nonyl), 1.44–1.26 (m, 24H, nonyl), 0.88–0.84 ppm (t, 6H, nonyl); ^{13}C NMR (CDCl_3): δ = 157.56, 154.65, 138.35, 136.64, 131.72, 128.02, 127.95, 127.45, 124.93, 124.19, 124.07 (Ar), 31.90, 30.46, 29.56, 29.46, 29.42, 29.33, 22.69, 14.12 ppm (nonyl); FAB-MS: m/z 748 (M^+); Anal. Calcd (%) for $\text{C}_{40}\text{H}_{48}\text{N}_2\text{S}_6$: C, 64.13; H, 6.46; N, 3.74. Found: C, 64.01; H, 6.38; N, 3.67.

Synthesis of 2,2'-Dibromo-5,5'-bis(bithienyl)-4,4'-dinonyl-2,2'-bithiazole (L2-2Br).

5,5'-Bis(bithienyl)-4,4'-dinonyl-2,2'-bithiazole (1.50 g, 2.00 mmol) was dissolved in a mixture of chloroform (60 mL) and acetic acid (10 mL). NBS (0.75 g, 4.20 mmol) was then added to the solution and the mixture was stirred for 1 h in the dark. The precipitate in the reaction mixture was filtered, washed with methanol, and dried to produce a red solid of **L2-2Br** (1.68 g, 93%). ^1H NMR (CDCl_3): δ = 7.07–7.05 (m, 4H, Ar), 7.00–6.98 (d, 2H, Ar), 6.95–6.93 (d, 2H, Ar), 2.95–2.91 (t, 4H, nonyl), 1.82–1.74 (m, 4H, nonyl), 1.41–1.33 (m, 24H, nonyl), 0.88–0.84 ppm (t, 6H, nonyl); ^{13}C NMR (CDCl_3): δ = 157.63, 154.82, 138.09, 137.19, 132.20, 130.75, 128.00, 127.26, 124.42, 124.10, 111.59 (Ar), 31.91, 30.48, 29.55, 29.46, 29.41, 29.39, 29.33, 22.70, 14.13 ppm (nonyl); FAB-MS: m/z 906 (M^+); Anal. Calcd (%) for $\text{C}_{40}\text{H}_{46}\text{N}_2\text{Br}_2\text{S}_6$: C, 52.97; H, 5.11; N, 3.09. Found: C, 52.92; H, 5.20; N, 2.99.

Synthesis of 5,5'-Bis(terthienyl)-4,4'-dinonyl-2,2'-bithiazole. The title compound was made following the same procedures as above by coupling 2-thienylmagnesium bromide with **L2-2Br**. Dark red solid. Yield: 76%. ^1H NMR (CDCl_3): δ = 7.27–7.25 (d, 2H, Ar), 7.18–7.13 (d, 6H, Ar), 7.10–7.08 (m, 4H, Ar), 7.05–7.02 (m, 2H, Ar), 2.97–2.93 (t, 4H, nonyl), 1.83–1.75 (m, 4H, nonyl), 1.44–1.26 (m, 24H, nonyl), 0.88–0.84 ppm (t, 6H, nonyl); FAB-MS: m/z 912 (M^+);

Anal. Calcd (%) for $C_{48}H_{52}N_2S_8$: C, 63.12; H, 5.74; N, 3.07. Found: C, 63.02; H, 5.66; N, 2.97.

Synthesis of 2,2'-Dibromo-5,5'-bis(terthienyl)-4,4'-dinonyl-2,2'-bithiazole (L3-2Br).

As above, bromination of 5,5'-bis(terthienyl)-4,4'-dinonyl-2,2'-bithiazole with NBS led to **L3-2Br** readily. Dark red solid. Yield: 56%. 1H NMR ($CDCl_3$): δ = 7.13–7.12 (d, 2H, Ar), 7.10–7.08 (m, 4H, Ar), 7.02–7.01 (d, 2H, Ar), 6.98–6.97 (d, 2H, Ar), 6.92–6.91 (d, 2H, Ar), 2.98–2.94 (t, 4H, nonyl), 1.82–1.74 (m, 4H, nonyl), 1.43–1.27 (m, 24H, nonyl), 0.88–0.84 ppm (t, 6H, nonyl); ^{13}C NMR ($CDCl_3$): δ = 157.45, 154.69, 138.35, 135.77, 135.66, 133.96, 132.00, 130.74, 128.15, 127.63, 124.65, 124.31, 124.03, 123.90, 111.32 (Ar), 31.91, 30.48, 29.56, 29.46, 29.43, 29.34, 22.70, 14.14 ppm (nonyl); FAB-MS: m/z 1070 (M^+); Anal. Calcd (%) for $C_{48}H_{50}N_2Br_2S_8$: C, 53.82; H, 4.70; N, 2.62. Found: C, 53.66; H, 4.62; N, 2.60.

Synthesis of L0-2TMS. To an ice-cooled mixture of **L0-2Br** (500 mg, 0.86 mmol) in freshly distilled triethylamine (20 mL) and dichloromethane (20 mL) solution mixture was added CuI (20.0 mg) and $Pd(OAc)_2$ (60.0 mg). After the solution was stirred for 30 min, trimethylsilylacetylene (0.30 mL, 2.00 mmol) was then added and the suspension was stirred for 30 min in an ice-bath before being warmed to room temperature. After reacting for 30 min at room temperature the mixture was heated to 50 °C for 24 h. The solution was then allowed to cool to room temperature and the solvent mixture was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel with a solvent combination of hexane/ CH_2Cl_2 (1:1, v/v) as eluent to provide **L0-2TMS** as a yellow solid (497 mg, 94%). IR (KBr): $\nu(C\equiv C)$ 2148 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 2.84–2.80 (t, 4H, nonyl), 1.74–1.69 (m, 4H, nonyl), 1.33–1.26 (m, 24H, nonyl), 0.88–0.85 (t, 6H, nonyl), 0.25 ppm (s, 18H, TMS); ^{13}C NMR ($CDCl_3$): δ = 164.01, 158.59, 115.44 (Ar), 105.42, 94.67 ($C\equiv C$), 31.89, 30.32, 29.53,

29.31, 29.15, 28.94, 22.68, 14.11 (nonyl), -0.23 ppm (TMS); FAB-MS: m/z 613 (M^+); Anal. Calcd (%) for $C_{34}H_{56}N_2S_2Si_2$: C, 66.61; H, 9.21; N, 4.57. Found: C, 66.70; H, 9.02; N, 4.45.

The same procedures were applied to prepare the other three bis-TMS derivatives from their corresponding dibromo derivatives.

L1-2TMS: Yellow solid. Yield: 92%. (Eluent: CH_2Cl_2 /hexane (1:1, v/v)). IR (KBr): $\nu(C\equiv C)$ 2139 cm^{-1} . 1H NMR ($CDCl_3$): δ = 7.19–7.18 (d, 2H, Ar), 7.02–7.01 (d, 2H, Ar), 2.93–2.89 (t, 4H, nonyl), 1.77–1.71 (m, 4H, nonyl), 1.40–1.25 (m, 24H, nonyl), 0.88–0.85 (t, 6H, nonyl), 0.26 ppm (s, 18H, TMS); ^{13}C NMR ($CDCl_3$): δ = 157.82, 155.21, 134.35, 133.18, 127.14, 127.00, 124.07, 100.96, 96.86 (Ar + $C\equiv C$), 31.89, 30.46, 29.52, 29.43, 29.41, 29.30, 22.68, 14.13 (nonyl), -0.20 ppm (TMS); FAB-MS: m/z : 777 (M^+); Anal. Calcd (%) for $C_{42}H_{60}N_2S_4Si_2$: C, 64.89; H, 7.78; N, 3.60. Found: C, 64.78; H, 7.69; N, 3.55.

L2-2TMS: Brown solid. Yield: 87%. (Eluent: CH_2Cl_2 /hexane (1:1, v/v)). IR (KBr): $\nu(C\equiv C)$ 2139 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.13–7.11 (m, 4H, Ar), 7.07–7.06 (d, 2H, Ar), 7.02–7.01 (d, 2H, Ar), 2.95–2.91 (t, 4H, nonyl), 1.82–1.74 (m, 4H, nonyl), 1.42–1.26 (m, 24H, nonyl), 0.88–0.85 (t, 6H, nonyl), 0.25 ppm (s, 18H, TMS); ^{13}C NMR ($CDCl_3$): δ = 157.57, 154.82, 137.98, 137.46, 133.52, 132.41, 128.05, 127.33, 124.65, 123.52, 122.34, 100.52, 97.20 (Ar + $C\equiv C$), 31.90, 30.51, 29.55, 29.47, 29.41, 29.37, 29.33, 22.69, 14.13 (nonyl), -0.18 ppm (TMS); FAB-MS: m/z : 942 (M^+); Anal. Calcd (%) for $C_{50}H_{64}N_2S_6Si_2$: C, 63.78; H, 6.85; N, 2.98. Found: C, 63.80; H, 6.77; N, 2.89.

L3-2TMS: Brown solid. Yield: 43%. (Eluent: CH_2Cl_2 /hexane (1:1, v/v)); IR (KBr): $\nu(C\equiv C)$ 2140 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.17–7.09 (m, 4H, Ar), 7.05–7.01 (m, 6H, Ar), 6.93–6.90 (m, 2H, Ar), 2.97–2.93 (t, 4H, nonyl), 1.83–1.76 (m, 4H, nonyl), 1.45–1.25 (m, 24H, nonyl), 0.88–0.84 (t, 6H, nonyl), 0.24 ppm (s, 18H, TMS); FAB-MS: m/z : 1106 (M^+); Anal.

Calcd (%) for $C_{58}H_{68}N_2S_8Si_2$: C, 63.00; H, 6.20; N, 2.53. Found: C, 62.88; H, 6.23; N, 2.44.

Synthesis of L0. A mixture of **L0-2TMS** (492 mg, 0.80 mmol) and K_2CO_3 (232 mg, 1.68 mmol) in MeOH/ CH_2Cl_2 (100 mL, 2:5, v/v) was stirred at room temperature overnight under nitrogen. Solvent was removed under reduced pressure to leave a dark residue. The residue was purified by column chromatography on silica gel using hexane/ CH_2Cl_2 (1:1, v/v) as eluent to afford a yellow solid of **L0** with an isolated yield of 93% (349 mg, 7.44 mmol). IR (KBr): $\nu(\equiv CH)$ 3255, $\nu(C\equiv C)$ 2098 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 3.60 (s, 2H, $C\equiv CH$), 2.86–2.82 (t, 4H, nonyl), 1.76–1.69 (m, 4H, nonyl), 1.32–1.25 (m, 24H, nonyl), 0.88–0.85 ppm (t, 6H, nonyl); ^{13}C NMR ($CDCl_3$): δ = 164.38, 159.00, 114.29 (Ar), 86.99, 74.13 ($C\equiv C$), 31.87, 30.29, 29.50, 29.33, 29.30, 29.16, 29.04, 22.67, 14.11 ppm (nonyl); FAB-MS: m/z : 468 (M^+); Anal. Calcd (%) for $C_{28}H_{40}N_2S_2$: C, 71.74; H, 8.60; N, 5.98. Found: C, 71.65; H, 8.65; N, 5.91.

The same procedures were applied to prepare the other three diethynyl derivatives **L1–L3** from their corresponding di-TMS derivatives.

L1: Yellow solid. Yield: 89%. (Eluent: CH_2Cl_2 /hexane (1:1, v/v)). IR (KBr): $\nu(\equiv CH)$ 3308, $\nu(C\equiv C)$ 2098 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.30–7.25 (t, 2H, Ar), 7.04–7.02 (d, 2H, Ar), 3.45 (s, 2H, $C\equiv CH$), 2.93–2.89 (t, 4H, nonyl), 1.80–1.72 (m, 4H, nonyl), 1.39–1.26 (m, 24H, nonyl), 0.88–0.85 ppm (t, 6H, nonyl); ^{13}C NMR ($CDCl_3$): δ = 157.91, 155.36, 134.70, 133.64, 126.96, 122.84 (Ar), 82.99, 76.41 ($C\equiv C$), 31.89, 30.46, 29.52, 29.44, 29.40, 29.30, 22.68, 14.12 ppm (nonyl); FAB-MS: m/z : 633 (M^+); Anal. Calcd (%) for $C_{36}H_{44}N_2S_4$: C, 68.31; H, 7.01; N, 4.43. Found: C, 68.11; H, 7.12; N, 4.33.

L2: Yellow solid. Yield: 83%. (Eluent: CH_2Cl_2 /hexane (1:1, v/v)). IR (KBr): $\nu(\equiv CH)$ 3292, $\nu(C\equiv C)$ 2096 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.19–7.17 (d, 2H, Ar), 7.14–7.13 (d, 2H, Ar), 7.08–7.07 (d, 2H, Ar), 7.04–7.02 (d, 2H, Ar), 3.42 (s, 2H, $C\equiv CH$), 2.96–2.92 (t, 4H, nonyl),

1.82–1.75 (m, 4H, nonyl), 1.41–1.26 (m, 24H, nonyl), 0.88–0.84 ppm (t, 6H, nonyl); ^{13}C NMR (CDCl_3): δ = 157.65, 154.91, 138.32, 137.26, 134.00, 132.58, 128.08, 127.28, 124.84, 123.51, 121.13 (Ar), 82.61, 76.68 ($\text{C}\equiv\text{C}$), 31.90, 30.49, 29.55, 29.46, 29.41, 29.38, 29.33, 22.69, 14.12 ppm (nonyl); FAB-MS: m/z : 797 (M^+); Anal. Calcd (%) for $\text{C}_{44}\text{H}_{48}\text{N}_2\text{S}_6$: C, 66.29; H, 6.07; N, 3.51. Found: C, 66.16; H, 5.88; N, 3.50.

L3: Brown solid. Yield: 49%. (Eluent: $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1, v/v)). IR (KBr): $\nu(\equiv\text{CH})$ 3307, $\nu(\text{C}\equiv\text{C})$ 2097 cm^{-1} ; ^1H NMR (CDCl_3): δ = 7.11–7.07 (m, 4H, Ar), 7.02–6.96 (m, 6H, Ar), 6.82–6.79 (m, 2H, Ar), 3.42 (s, 2H, $\text{C}\equiv\text{CH}$), 2.96–2.92 (t, 4H, nonyl), 1.82–1.75 (m, 4H, nonyl), 1.41–1.26 (m, 24H, nonyl), 0.88–0.84 ppm (t, 6H, nonyl); FAB-MS: m/z : 961 (M^+); Anal. Calcd (%) for $\text{C}_{52}\text{H}_{52}\text{N}_2\text{S}_8$: C, 64.96; H, 5.45; N, 2.91. Found: C, 64.88; H, 5.54; N, 3.02.

X-Ray crystallography: X-Ray diffraction data were collected at 293 K using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) on a Bruker Axs SMART 1000 CCD diffractometer. The collected frames were processed with the software SAINT^[S1] and an absorption correction (SADABS)^[S2] was applied to the collected reflections. The structure was solved by the Direct or Patterson methods (SHELXTL)^[S3] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2 . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were refined anisotropically. Crystal data for **L2-2Br**·MeOH: $\text{C}_{41}\text{H}_{50}\text{N}_2\text{Br}_2\text{OS}_6$ M_w = 939.01, monoclinic, space group $P2_1/c$, a = 14.653(1), b = 4.1102(4), c = 37.163(4) Å, β = 92.642(2)°, V = 2235.8(4) Å³, Z = 2, ρ_{calcd} = 1.395 mg m^{-3} , $\mu(\text{MoK}\alpha)$ = 2.126 mm^{-1} , $F(000)$ = 968. 10008 reflections measured, of which 3843 were unique (R_{int} = 0.0348). Final R_1 = 0.0590 and wR_2 = 0.1428 for 2493 observed reflections with $I > 2\sigma(I)$.

References:

- [S1] SAINT+, ver. 6.02a, Bruker, Analytical X-ray System, Inc., Madison, WI, **1998**.
- [S2] Sheldrick, G. M. SADABS, Empirical Absorption Correction Program, University of Göttingen, Germany, **1997**.
- [S3] Sheldrick, G. M. SHELXTLTM, Reference Manual, ver. 5.1, Madison, WI, **1997**.

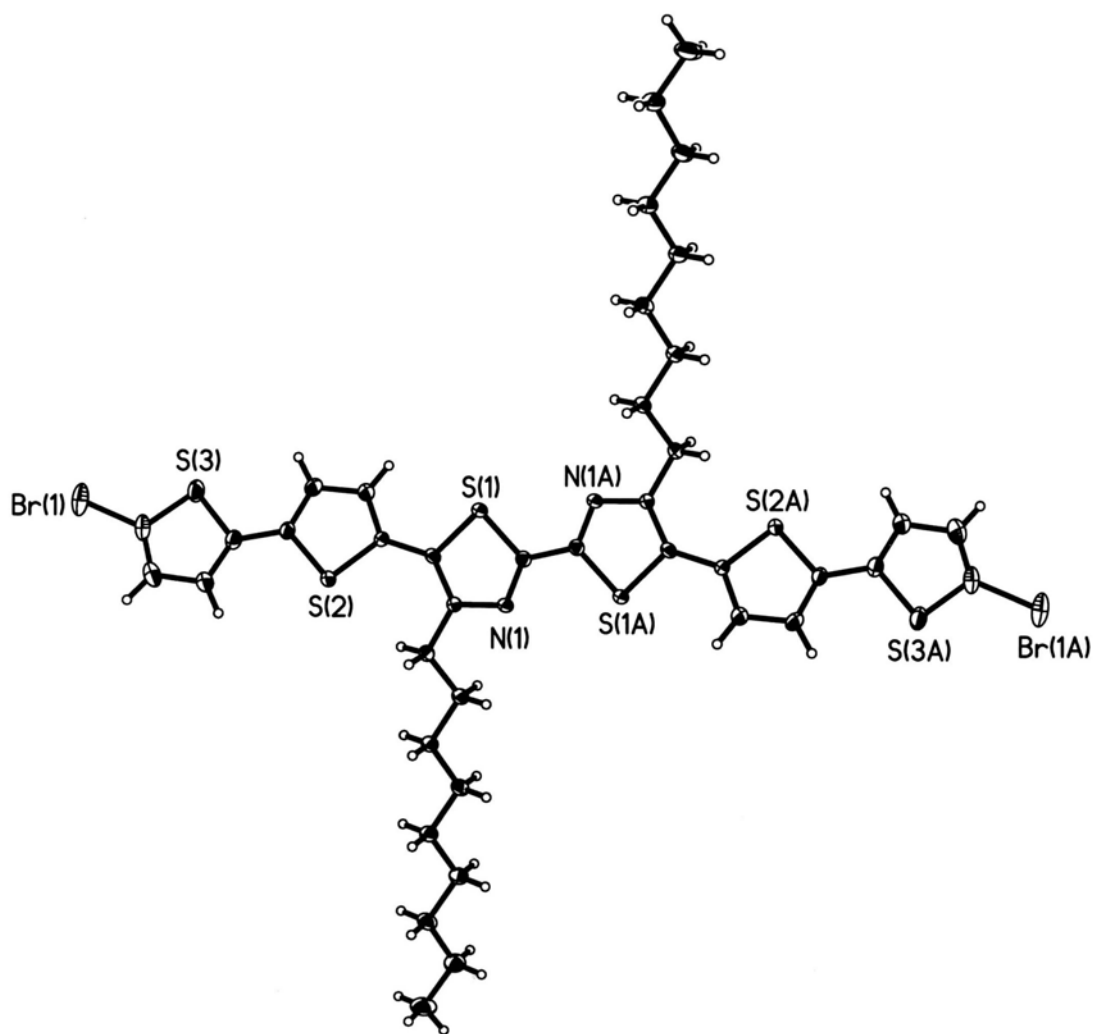


Figure S1. X-ray crystal structure of **L2-2Br**. Labels on carbon atoms are omitted for clarity.

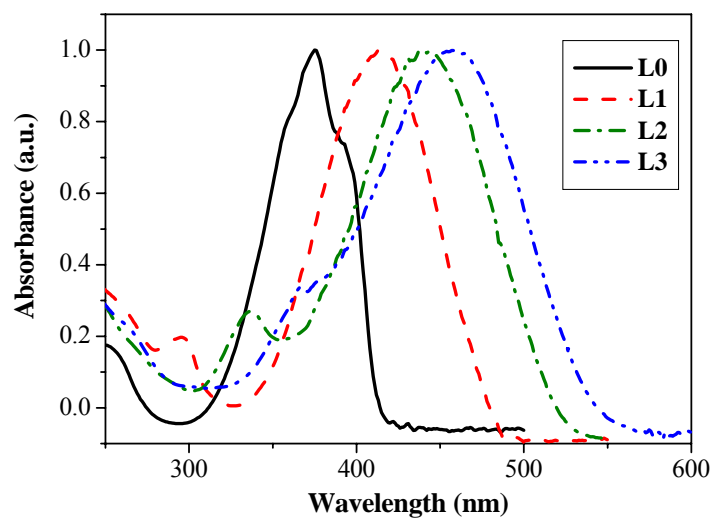


Figure S2. Absorption spectra of **L0–L3** at 293 K.

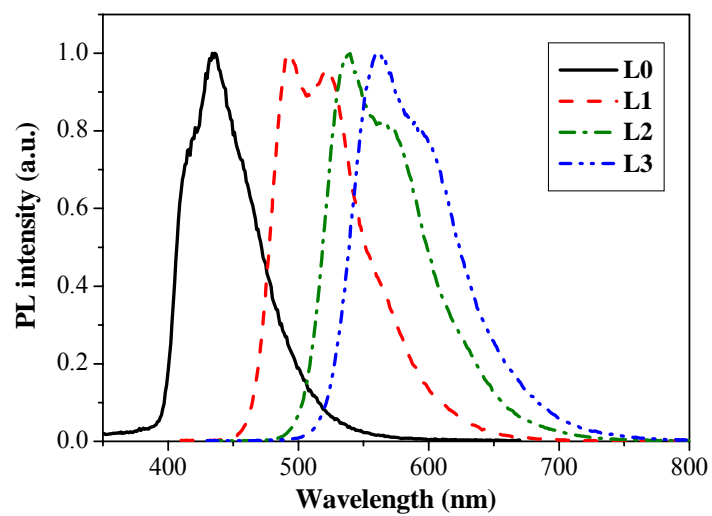


Figure S3. PL spectra of **L0–L3** at 293 K.

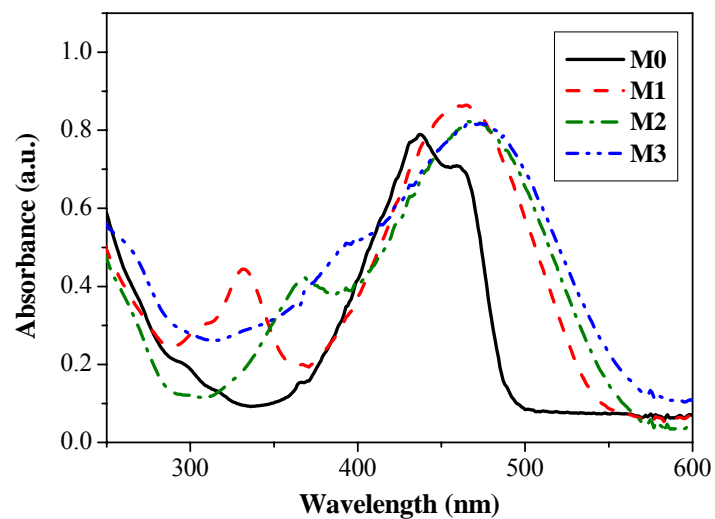


Figure S4. Absorption spectra of **M0–M3** at 293 K.

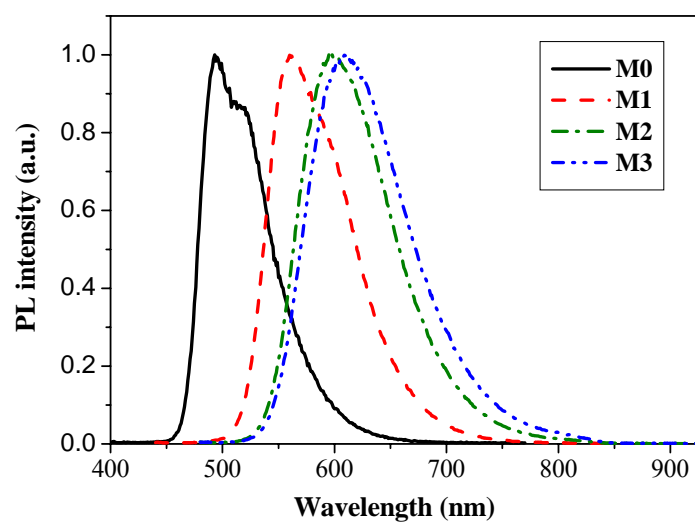


Figure S5. PL spectra of **M0–M3** at 293 K.

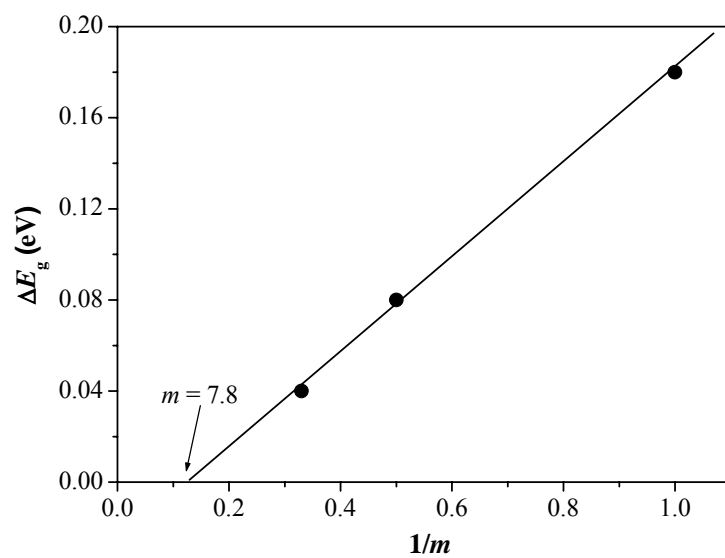
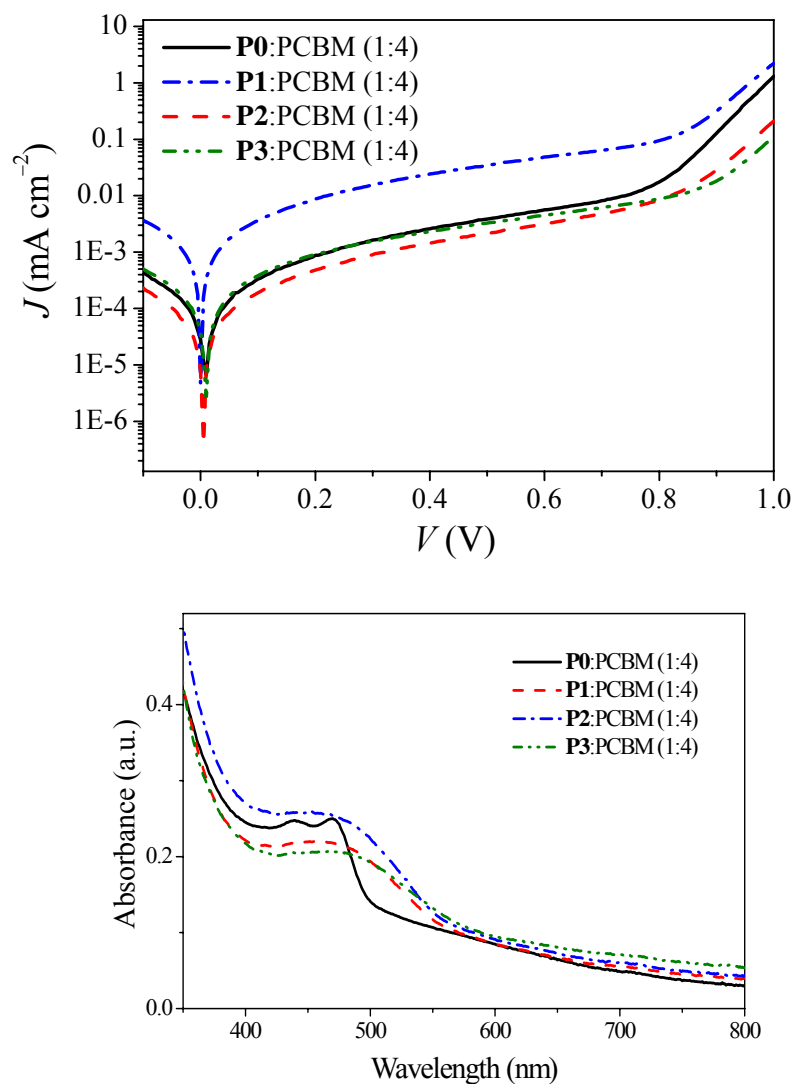


Figure S6. Relationship of ΔE_g and $1/m$ for **P0–P3**.



b)

Figure S7. a) J - V curves of solar cells with **P0**–**P3**:PCBM (1:4) active layers in the dark. b) Absorption of **P0**–**P3**:PCBM (1:4) films. The film thicknesses were in the range ~60–80 nm.

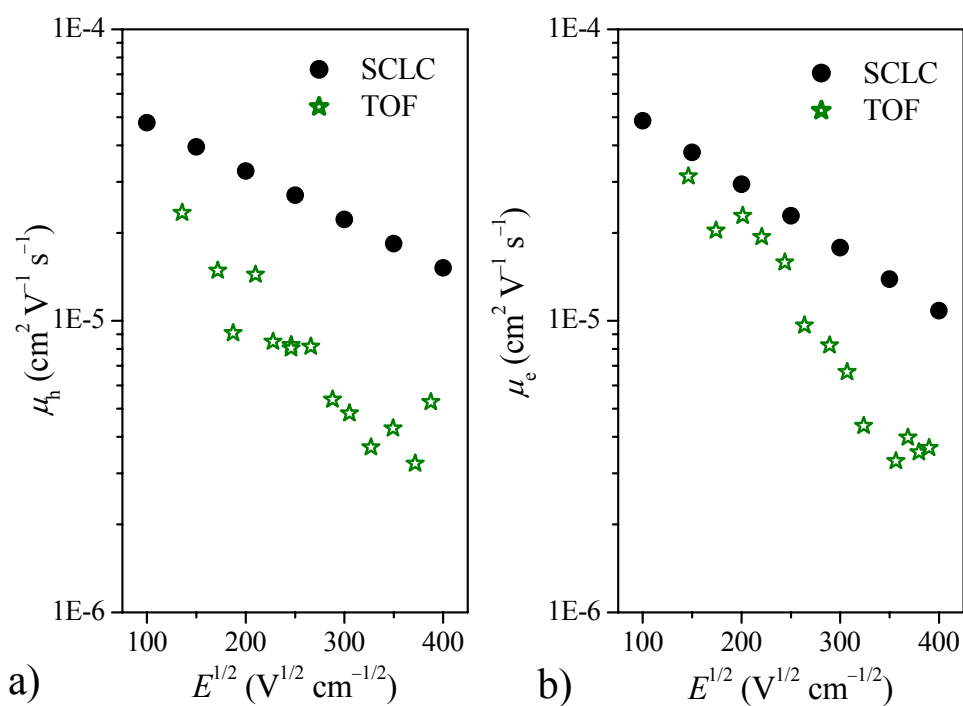


Figure S8 Comparison between a) hole and b) electron mobilities of **P0**:PCBM blends obtained from the SCLC and TOF measurements.

Table S1. Absorption and emission data for diethynyl ligands.

Ligand	Absorption λ_{abs} (nm) ^[a]	Emission λ_{em} at 290 K (nm) ^[b]	Φ (%) ^[c]	E_g (eV) ^[d]
L0	375 (2.47)	436 (1.31)	7.1	3.00
L1	296 (5.37) 413 (27.4)	493 522 (1.08)	28.1	2.55
L2	337 (5.95) 440 (22.1)	539 (1.28) 564*	22.8	2.38
L3	367 (5.92) 459 (17.4)	562 (1.05) 590*	17.9	2.29

[a] In CH₂Cl₂ at 290 K. Extinction coefficients (10⁴ M⁻¹ cm⁻¹) are shown in parentheses.

[b] Lifetimes (ns) shown in parentheses were measured in CH₂Cl₂ solutions.

[c] Fluorescence quantum yields were measured in CH₂Cl₂ solutions.

[d] Determined from the onset absorption in the UV-Vis spectra.

Asterisk refers to a weak or shoulder peak.

Table S2. Absorption and emission data for **M0–M3**.

Compound	Absorption λ_{abs} (nm) ^[a]	Emission λ_{em} (nm) ^[b]		Φ (%) ^[c]	E_g (eV) ^[d]
		290 K	77 K		
M0	437 (5.1) 459* (4.6)	494 (2.22) 517*	488 (2.46) 519	7.2	2.54
M1	332 (4.0) 463 (7.2)	560 (1.70)	547 (0.78) 578*	9.4	2.29
M2	368 (7.3) 469 (12.8)	600 (1.12)	575 (1.11)	6.3	2.23
M3	399* (15.7) 473 (24.9)	610 (1.16)	589 (1.16)	4.1	2.21

[a] In CH₂Cl₂ at 290 K. Extinction coefficients (10⁴ M⁻¹ cm⁻¹) are shown in parentheses.

[b] Lifetimes (ns) shown in parentheses were measured in CH₂Cl₂ solutions.

[c] Fluorescence quantum yields shown in parentheses were measured in CH₂Cl₂ relative to quinine sulfate (Φ = 0.54).

[d] Determined from the onset absorption in the UV-Vis spectra.

Asterisk refers to a weak or shoulder peak.

Table S3. Positive solvatochromism of the PL data (in nm) for **P2** and **P3**.

	P2	P3
Toluene	539	566
THF	548	582
CH ₂ Cl ₂	563	618