Supplementary Information for

Synthesis of Low Bandgap Polymers Based on Thienoquinodimethane Units and Their Applications to Bulk Heterojunction Solar Cells

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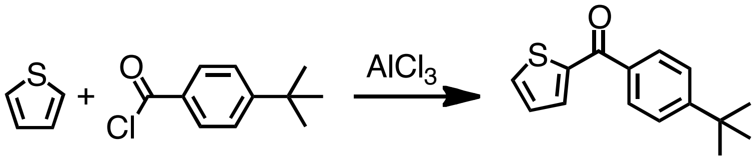
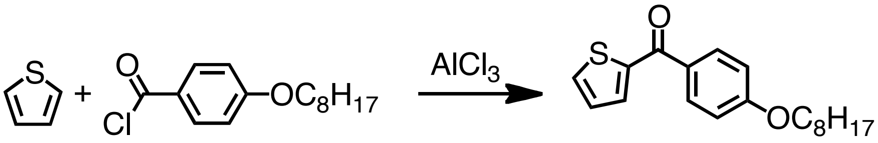
Synthesis



4-(*t*-Butyl)phenyl 2-thienyl ketone. Anhydrous aluminium chloride (10.3 g, 0.077 mol) was added in four portions to an ice-cooled solution of 4-(*t*-butyl)benzoyl chloride (12.8 g, 0.065 mol) and thiophene (5.0 g, 0.060 mol) in anhydrous dichloromethane (50 mL) under argon protection. The reaction was stirred at room temperature overnight. The reaction was quenched with water, the mixture was made acid with 37% HCl (1.3 mL) and extracted with chloroform. The organic layer was washed with brine and then the solvent was evaporated. The crude product was recrystallized with hexane. After drying under vacuum, pure product was obtained as pale yellow crystals. Yield 12.4 g (85%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$; Me_4Si): 7.83 (d, 2H), 7.70 (dd, 1H), 7.69 (dd, 1H), 7.51 (d, 2H), 7.16 (t, 1H), 1.37 (s, 9H). IR (ATR): cm^{-1} 3086, 3058, 3026, 2958, 2931, 2871, 2855, 1700, 1634, 1603, 1560, 1539, 1516, 1507, 1495, 1459, 1453, 1379, 1031, 738, 697. HRMS (*m*/*z*): calcd for $C_{15}H_{16}OS$, 244.0992; found 245.0985 [M + H].



4-(Octyloxy)phenyl 2-thienyl ketone. To a solution of thiophene (1.59 mL, 20 mmol) and *p*-(octyloxy)benzoyl chloride (5.4 g, 20 mmol) in dichloromethane (17 mL), anhydrous aluminium chloride (2.7 g, 0.020 mol) was added in an ice bath. The mixture was stirred at room temperature for 10 h. Then HCl (aqueous 1 M solution, 38 mL) was added slowly, and the organic phase was separated. The aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated. The crude product was passed through a silica gel column with dichloromethane/hexane (1:1, v/v) to give the product as pale yellow powder. Yield 5.9 g (93%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$; Me_4Si): 7.89 (d, 2H), 7.68 (dd, 1H), 7.65 (dd, 1H), 7.16 (t, 1H), 6.97 (d, 2H), 4.04 (t, 2H), 1.82 (p, 2H), 1.48-1.30 (10H), 0.88 (t, 3H). IR (ATR): cm^{-1} 3111, 3068, 2944, 2925, 2857, 1623, 1603, 1573, 1508, 1470, 1419, 1296, 1257, 1175, 1135, 1058, 1025, 1000, 884, 848, 760, 718, 638 cm^{-1}. HRMS (*m*/*z*): calcd for $C_{19}H_{24}O_2S$, 317.1570; found 317.1563.

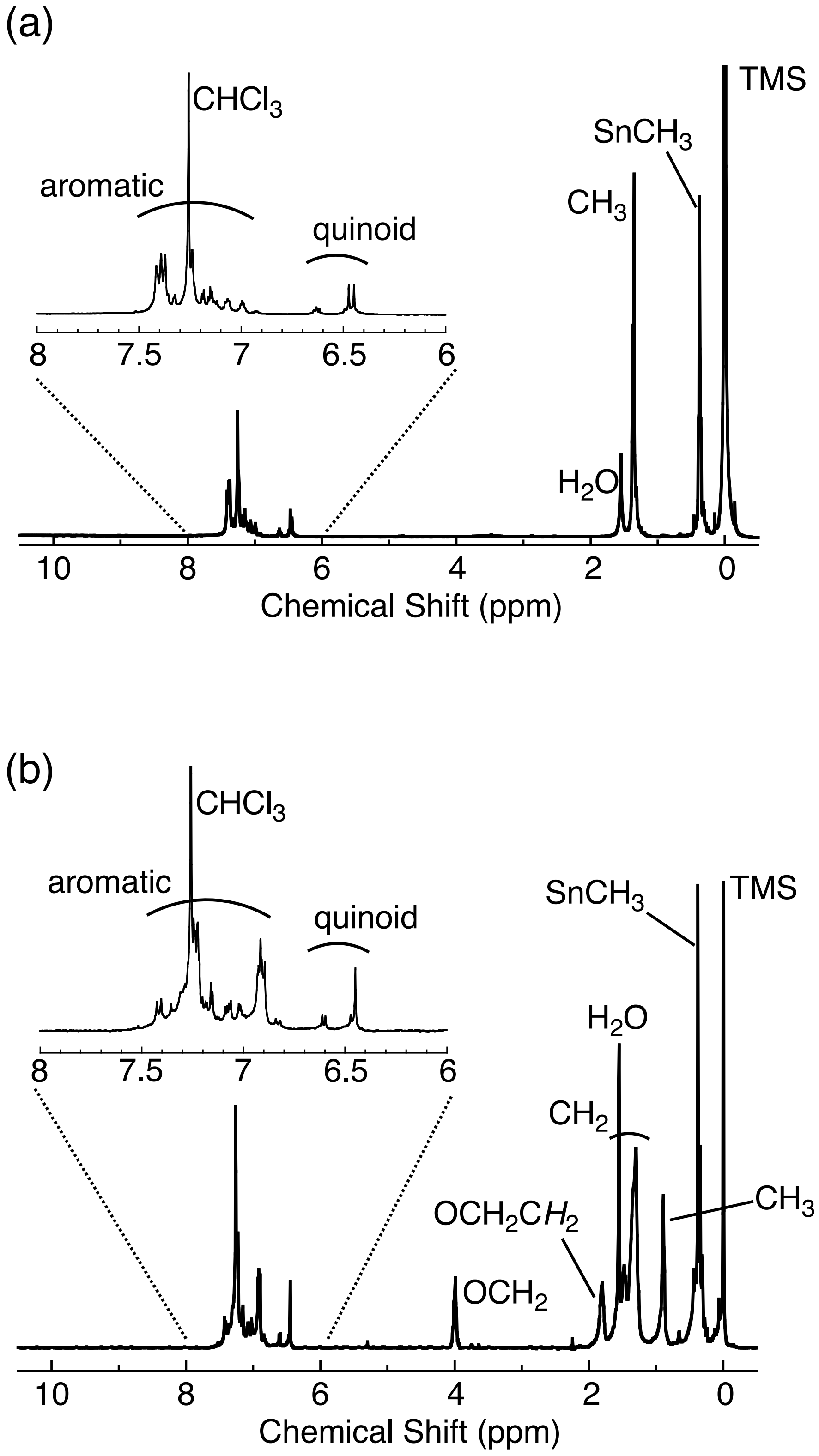


Fig. S1 ^{1}H NMR spectra of (a) **3a** and (b) **3b** in $CDCl_3$.

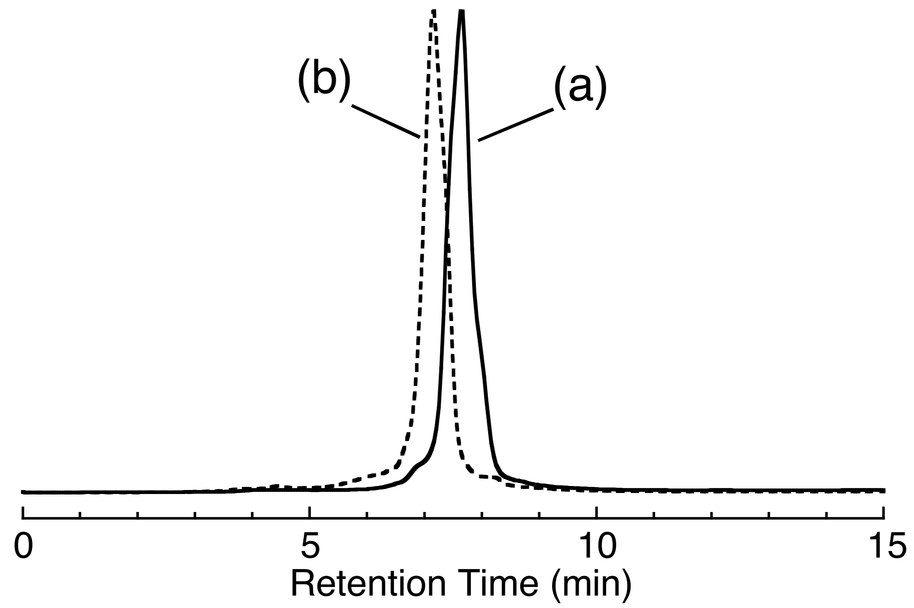


Fig. S2 GPC traces of (a) **3a** (solid line) and (b) **3b** (dotted line) in $CHCl_3$. The molecular weights of **3a** and **3b** at the peak tops correspond to 600 and 900, respectively, calibrated with polystyrene standards. They are significantly smaller than the molecular weights of 864 and 1009, respectively, indicating the compact molecular sizes of **3a** and **3b**.

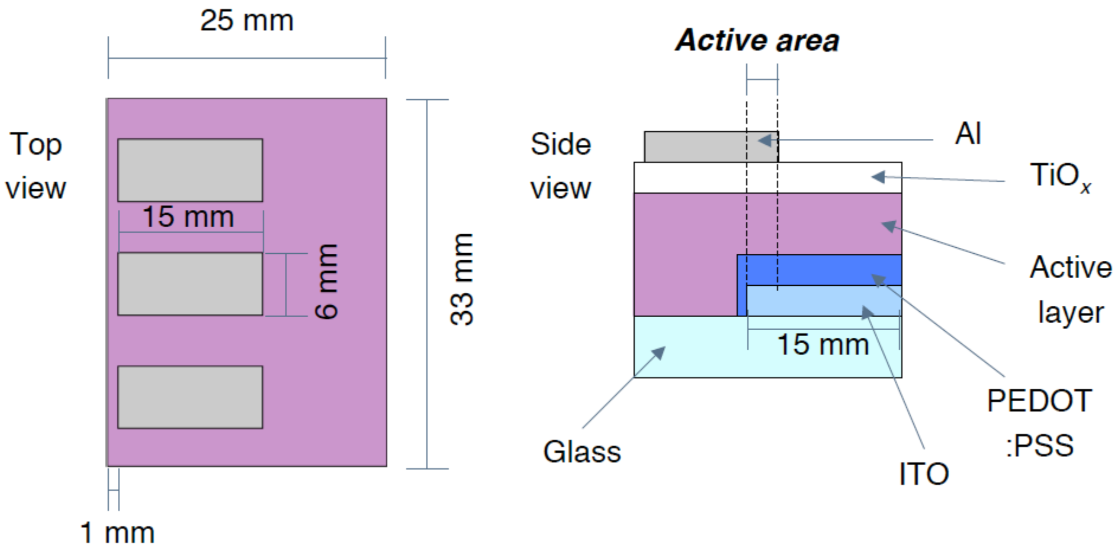


Fig. S3 Schematic illustrations of top and side views of the ITO/PEDOT:PSS/polymer:PCBM/TiO$_x$/Al device.

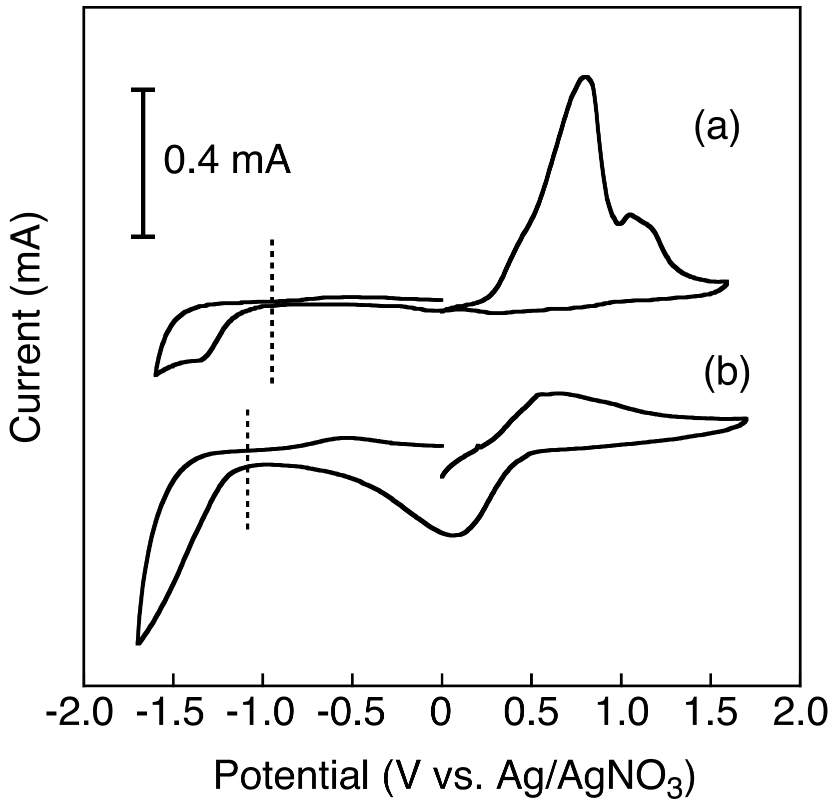


Fig. S4 Cyclic voltammograms of (a) **PQD1** and (b) **PQD2** films measured in acetonitrile containing 0.1 M n-Bu$_4$N$^+$PF$_6^-$ as a supporting electrolyte. ITO working electrodes coated with polymer films, Ag/AgNO$_3$ (0.01 M in acetonitrile) reference electrode, and Pt wire counter electrode were employed. Decamethylferrocene/decamethylferrocenium (+0.15 V vs. NHE) was used as a standard for all measurements. The vertical dashed lines show the onsets of the first reduction potentials.

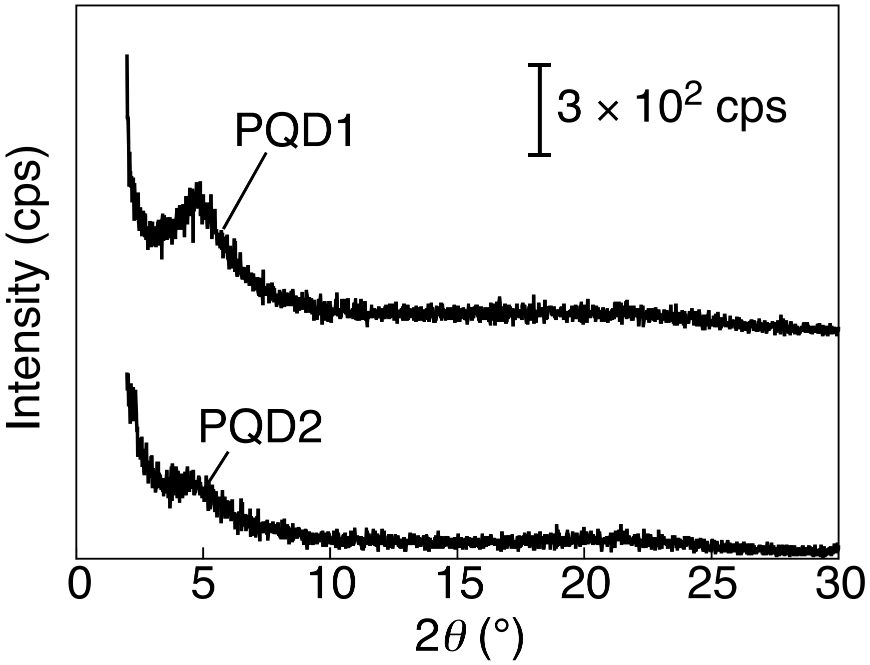


Fig. S5 In-plane XRD patterns of **PQD1** and **PQD2** films.