Supporting Information for

Donor–Acceptor-Type Low Bandgap Polymer Carrying Phenylazomethine Moiety as a Metal-Collecting Pendant Unit: Open-Circuit Voltage Modulation of Solution-Processed Organic Photovoltaic Devices Induced by Metal Complexation

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1. Experimental Methods

All the chemicals were purchased from Kanto Chemical, Wako Pure Chemical Industries, Tokyo Kasei and Aldrich and used as received, unless otherwise noted. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F–254). ¹H–NMR spectra were obtained at 400 MHz with an AL-400 (JEOL) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane. Electronic absorption spectra were recorded on a Shimadzu model UV3150 spectrophotometer. The molecular weight of polymers were estimated by GPC on a Senshu Scientific SSC7110, and polystyrene was used as the standard (*o*-dichlorobenzene as the eluent at 90 $^{\circ}$ C). Cyclic voltammetry experiments were performed with a BAS-612A electrochemistry analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, an auxiliary platinum electrode, and a nonaqueous Ag/AgNO₃ reference electrode. The solvent in all experiments was acetonitrile, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potentials reported are referenced to Fc/Fc⁺ external and are not corrected for the junction potential.

2. Synthesis of Monomers

The compound **2** was prepared according to the literature procedures.

Synthesis of Compound 1. To a solution of 4,4'-dihydroxybenzophenone (4.28 g, 20 mmol, potassium carbonate (6.63 g, 48 mmol) in N,N-dimethylformamide (80 mL) in a dried flask was added dropwise 7.6 mL (44 mmol) of 2-ethylhexylbromide. The mixture was stirred at 70 °C for 15 h. The resulting mixture was poured into water and extracted with dichloromethane three times. The organic layer was dried over anhydrous Na₂SO₄, and evaporated to dryness to give crude product. The crude mixture was purified with

silica gel column chromatography using dichloromethane/hexane = 1/4 as eluent to give **1** as colorless oil (5.96 g, 68%). ¹H NMR (CDCl₃, 400 MHz): δ 7.78 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 3.92 (d, *J* = 6.0 Hz, 4H), 1.76–1.70 (m, 2H), 1.60–1.20 (m, 16H), 0.96–0.91 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 194.49, 162.66, 132.18, 130.50, 113.90, 70.67, 39.29, 30.47, 29.05, 23.82, 23.02, 14.06, 11.09. FAB-MS: *m/z* 439 [M+H]⁺. Anal. Calcd. for C₂₉H₄₂O₃: C, 79.41; H, 9.65. found: C, 79.10; H, 9.42.

Synthesis of Compound 3. 1 (0.719 g, 1.64 mmol), 2 (0.750 mg, 1.80 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.303 g, 2.70 mmol) were dissolved in chlorobenzene (12 mL) and heated to 60 °C. TiCl₄ (0.15 mL, 1.35 mmol) dissolved in 2 mL of chlorobenzene was added dropwise, and the addition funnel was then rinsed with 2 mL of chlorobenzene. The mixture was then heated to 120 °C and stirred for 4 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness and the crude mixture was purified with silica gel column chromatography using dichloromethane/hexane = 1/1 as eluent to give 3 as yellow solid (1.23 g, 90%). ¹H NMR (CDCl₃, 400 MHz): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.37 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.36 (s, 2H) 7.25 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.96–6.85 (m, 4H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.92 (d, *J* = 5.4 Hz, 2H), 1.76–1.72 (m, 2H), 1.60–1.20 (m, 16H),

0.97–0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 168.56, 161.82, 159.86, 152.22, 142.20, 132.17, 131.57, 131.31, 130.61, 127.76, 127.51, 123.29, 122.95, 121.43, 121.37, 119.80, 114.09, 113.81, 113.08, 70.65, 70.60, 39.39, 39.30, 30.49, 29.10, 29.07, 23.82, 23.04, 14.08, 11.15, 11.10. FAB-MS: *m/z* 838 [M+H]⁺. Anal. Calcd. for C₄₇H₅₂Br₂N₂O₂: C, 67.46; H, 6.26. found: C, 67.72; H, 6.01.

Synthesis of Compound 4. A flask was charged with 3 (0.991 g, 1.18 mmol), bis(pinacolato)diboron 2.84 (0.722)mmol), g, [1,1'-bis(diphenylphosphino)ferrocene]palladium dichloride dichloromethane adduct (0.136 g, 0.166 mmol), potassium acetate (0.814 g, 8.29 mmol) and dehydrated 1,4-dioxane (14 mL). The resultant mixture was degassed and heated at 90 °C. After 14 h, the reaction mixture was evaporated to dryness and the crude mixture was purified with silica gel column chromatography using ethyl acetate/hexane = 1/8 to 1/3 as eluent to give **4** as yellow solid (0.882 g, 80%). ¹H NMR (CDCl₃, 400 MHz): δ 8.14 (d, J = 8.0Hz, 2H), 7.76-7.74 (m, 4H), 7.70 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.00-6.93 (m, 4H), 6.88 (d, J = 8.8 Hz, 2H), 3.92 (d, J = 5.8 Hz, 2H), 3.83 (d, J = 5.6 Hz, 2H), 1.77–1.70 (m, 2H), 1.60-1.20 (m, 16H), 1.36 (s, 24H), 0.97–0.87 (m, 12H).¹³C NMR (CDCl₃, 100 MHz): δ 167.79, 161.64, 159.84, 151.09, 141.42, 132.70, 132.13, 131.76, 131.28, 128.32, 127.74, 127.68, 125.98, 125.61, 125.26, 122.83, 119.83, 116.40, 114.03, 113.88, 83.72, 70.62, 70.51, 39.31, 30.49, 30.40, 29.06, 25.01, 24.89, 23.83, 23.71, 23.04, 23.00, 14.09, 14.05, 11.10, 11.08. FAB-MS: *m/z* 932 [M+H]⁺. Anal. Calcd. for C₅₉H₇₆B₂N₂O₆: C, 76.13; H, 8.23. found: C, 76.35; H, 8.03.



Figure S1. ¹H NMR spectrum of 1 in CDCl₃.



Figure S2. ¹³C NMR spectrum of 1 in CDCl₃.



Figure S3. ¹H NMR spectrum of 3 in CDCl₃.



Figure S4. ¹³C NMR spectrum of 3 in CDCl₃.



Figure S5. ¹H NMR spectrum of 4 in CDCl₃.



Figure S6. ¹³C NMR spectrum of 4 in CDCl₃.

3. Synthesis of PImCDTBT.

Synthesis. A 200 mL flask was charged with 4 (0.107 g, 0.115 mmol), 5 (0.0525 g, 0.115 mmol), tetrakis(triphenylphosphine)palladium (2.6 mg, 2.3 µmol), Aliquat 336 (4 mg), aqueous 2M Na₂CO₃ (1 mL) and toluene (2 mL). The resultant mixture was degassed and heated at 80 °C. After 72 h, bromobenzene (0.1 mL) was added to the reaction then 4 hours later, phenylboronic acid (20 mg, 0.110 mmol) was added and the reaction heated overnight to complete the end-capping reaction. The polymer was precipitated in methanol, then collected by filtration and washed with water and methanol to yield the crude polymer. The polymer was further purified by washing via Soxhlet extraction with methanol (3 h), acetone (12 h), hexane (12 h), toluene (24 h) and chloroform (24 h). The chloroform fraction was evaporated and reprecipitated into methanol. The polymer was filtered and washed with methanol and acetone, then dried in vacuo to give product as a deep blue solid (0.059 g, 52%). ¹H NMR (o-dichlorobenzene-d₄, 80 °C, 400 MHz): δ 8.43–6.89 (br, 40H), 4.15–3.89 (br, 8H), 2.13–0.69 (br, 60H).



Figure S7. ¹H NMR spectrum of **PImCDTBT** in *o*-dichlorobenzene- d_4 at 80 °C.

Estimation of the molecular weight of PImCDTBT from the ¹H NMR spectrum.



Figure S8. Structure of PImCDTBT for estimation of the molecular weights.

The plausible structure for **PImCDTBT** structure is described in Figure S8. The integration ratio of signals (aromatic to alkoxy proton) is (a) 6.8, (b) 7.3, (c) 6.3, and (d) 8.0, respectively. The integration ratio for (d) is reasonable for experimental integration ratio and molecular weight.

4. Complexation Behavior of PImCDTBT and Monomers.



Figure S9. Differential UV-vis spectral changes of **PImCDTBT** on stepwise addition of $SnCl_2$ in CH₃CN/CHCl₃ = 1/4.



Figure S10. UV-vis spectral changes of the monomers, (a) 4 + x equiv. of SnCl₂ and (b) 4,7-dithien-5'-yl-2,1,3-benzothiadiazole + *x* equiv. of SnCl₂, in CH₃CN/CHCl₃ = 1/4.



Figure S11. a) Cyclic voltammogram and differential pulse voltammogram and b) its enlargement of the cast film of **PImCDTBT** complexed with an equimolar amount of SnCl₂ measured in acetonitrile at scan rate of 100 mV/sec with Bu_4NPF_6 (0.1 mol/L) as electrolyte. The film was prepared by spin-coating chloroform solution on the working electrode.

5. Device Characteristics.

Table S1. Device Characteristics (for the Best Device) Using **PImCDTBT** with n wt% SnCl₂

n	$J_{\rm SC}$ / mA/cm ²	$V_{ m OC}$ / V	FF	η / %
0	2.12	0.46	0.26	0.25
1	1.88	0.52	0.24	0.24
5	1.65	0.52	0.24	0.18

Table S2. Average Device Characteristics and their Standard Deviation (Numbers in Parentheses) for 8 Different Devices Using **PImCDTBT** with n wt% SnCl₂

n	$J_{\rm SC}$ / mA/cm ²	$V_{ m OC}$ / V	FF	η / %
0	1.94 (0.13)	0.46 (0.00)	0.25 (0.01)	0.22 (0.02)
1	1.72 (0.16)	0.50 (0.02)	0.25 (0.01)	0.21 (0.03)
5	1.50 (0.12)	0.51 (0.01)	0.22 (0.00)	0.17 (0.02)