

Supporting Information

Dithieno[3,2-*b*:2',3'-*d*]arsole-containing conjugated polymers in organic photovoltaic devices

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Contents

1. Experimental details
 - a. General considerations
 - b. Synthesis of P1 and P2
 - c. Device fabrications conditions
2. NMR spectra of polymers
 - a. P1
 - b. P2
3. Cyclic voltammograms
4. Differential scanning calorimetry traces
5. Alternate photovoltaic performances
6. References

Experimental Details

General Considerations

4,8-Bis[5-(2-ethylhexyl)thiophen-2-yl]-2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b'*]dithiophene and 4,8-bis[5-(2-butyloctyl)thiophen-2-yl]-2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b'*]thiophene were purchased from Solarmer Materials Inc. Other reagents were purchased from Sigma Aldrich and VWR and used without further purification. Compound **2** was prepared as previously reported.¹ All reactions were performed in oven-dried glassware under argon using Schlenk techniques. ¹H spectra were recorded using Bruker AV-400 spectrometers (400 MHz) at 298 K unless otherwise stated. Microwave reactions were carried out in a Biotage Initiator (v. 2.3). UV-visible spectroscopy was performed using a UV-1800 Shimadzu UV-vis spectrometer for both solution and thin-film samples. Thin films of the polymers were prepared by spin coating 5 mg ml⁻¹ solutions of polymer in chlorobenzene at 1000 rpm for 60 s. Molecular weights (M_n , M_w , \bar{D}) were measured using an Agilent Technologies 1200 series GPC at 80 °C, using chlorobenzene as an eluent with two PL mixed B columns in series. The column was calibrated using narrow polydispersity polystyrene standards. Cyclic voltammetry (CV) was performed in a standard three-electrode setup with polymer film on FTO as the working electrode, a Pt mesh as the counter electrode and a Ag wire as the reference electrode. The working electrodes were prepared by spin coating a 10 mg ml⁻¹ solution of polymer in chlorobenzene onto FTO-coated glass (supplied by Sigma Aldrich, ~7 Ω/sq) at 1000 rpm for 60 s. Voltammograms were measured using a 0.1 M tetrabutylammonium hexafluorophosphate ((TBA)PF₆) solution in acetonitrile as an electrolyte, at a scanning rate of 0.05 V s⁻¹. Redox potentials were calibrated against a standard ferrocene/ferrocenium (FOC) system, assuming the energy level of FOC to be 4.8 eV below vacuum. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.5. Films were spun-cast onto glass and annealed

Synthesis of P1

An oven-dried high-pressure microwave tube was charged with **2** (100.0 mg, 0.123 mmol), **3** (125.3 mg, 0.123 mmol), and Pd(PPh₃)₄ (3.0 mg, 0.002 mmol). The tube was sealed with a septum and flushed with Ar, after which degassed chlorobenzene was added (2 ml). The mixture was thoroughly degassed with Ar, after which the inlet was removed. The vial was then placed in a microwave reactor and heated as follows: 4 min at 100 °C, 120 °C, and 140 °C, 20 min at 160 °C, and 60 min at 180 °C. After cooling to room temperature, the resulting polymer was precipitated into methanol and filtered into a Soxhlet thimble. The polymer was extracted (Soxhlet) with methanol, acetone, and hexane in that order. The hexane fraction was concentrated under reduced pressure and the resulting polymer was dissolved in chlorobenzene, warmed to 50 °C and stirred in the presence of diethylammonium diethyldithiocarbamate (10 mg) for 1 h. The solution was concentrated in vacuo, dissolved in a minimal amount of hot chlorobenzene and the polymer collected by re-precipitation into methanol followed by vacuum filtration. After drying under vacuum, **P1** was collected (154.5 mg, 94%). GPC (chlorobenzene): M_n 14,000 g/mol, M_w 27,000 g/mol, \bar{D} 1.93. ¹H NMR (400 MHz, 323 K, CDCl₃) δ 7.77 – 7.50 (broad m, 2H), 7.38 – 7.27 (broad m, 5H), 7.26 – 7.19 (broad m, 2H), 6.96 – 6.81 (broad m, 2H), 2.93 – 2.70 (broad m, 8H), 1.82 – 1.65 (broad m, 2H), 1.59 – 1.03 (broad m, 72H), 0.96 – 0.83 (broad m, 18H). Anal. Calcd. for C₈₀H₁₁₁AsS₆: C, 71.70; H, 8.35. Found: C, 70.42; H, 8.52.

Synthesis of P2

An oven-dried high-pressure microwave tube was charged with **2** (100.1 mg, 0.123 mmol), **4** (111.1 mg, 0.123 mmol), and Pd(PPh₃)₄ (3.0 mg, 0.002 mmol). The tube was sealed with a septum and flushed with Ar, after which degassed chlorobenzene was added (2 ml). The mixture was thoroughly degassed with Ar, after which the inlet was removed. The vial was then placed in a microwave reactor and heated as follows: 4 min at 100 °C, 120 °C, and 140 °C, 20 min at 160 °C, and 60 min at 180 °C. After cooling to room temperature, the resulting polymer was precipitated into methanol and filtered into a Soxhlet thimble. The polymer was extracted (Soxhlet) with methanol, acetone, hexane, and chloroform in that order. The hexane and chloroform fractions were concentrated under reduced pressure and the resulting polymer samples were dissolved in chlorobenzene, warmed to 50 °C and stirred in the presence of diethylammonium diethyldithiocarbamate (10 mg) for 1 h. The solutions were then concentrated in vacuo, dissolved in minimal amounts of hot chlorobenzene and the polymer samples collected by re-precipitation into methanol followed by vacuum filtration. After drying under vacuum, two fractions of **P2** were collected: hexane (126.5 mg, 83.7%), GPC (chlorobenzene): M_n 20,000 g/mol, M_w 37,200 g/mol, \bar{D} 1.86; chloroform (11 mg, 7.3%), GPC (chlorobenzene): M_n 30,000 g/mol, M_w 50,400 g/mol, \bar{D} 1.68. ¹H NMR (400 MHz, 323 K, CDCl₃) δ 7.77 – 7.47 (broad m, 2H), 7.38 – 7.19 (broad m, 7H), 6.95 – 6.83 (broad m, 2H), 2.94 – 2.66 (broad m, 8H), 1.75 – 1.64 (broad m, 2H), 1.56 – 1.05 (broad m, 56H), 1.00 – 0.81 (broad m, 18H). Anal. Calcd. for C₇₂H₉₅AsS₆: C, 70.43; H, 7.80. Found: C, 70.46; H, 7.57.

Device Fabrication Conditions

The solar cell devices were fabricated to have a conventional structure of glass/indium tin oxide (ITO)/PEDOT:PSS/**P1** or **P2**:PC₇₁BM/Cs/Al. The ITO-coated glass substrates were cleaned with detergent, deionized water, acetone, and isopropanol in a sonication bath. The glass/ITO substrates were then exposed to UV-ozone for 8 min. Subsequently, a PEDOT:PSS (Clevios P VP Al 4083, filtered using 0.45 μ m PVDF) layer with a thickness of 40 nm was spin-coated and the glass/ITO/PEDOT:PSS substrates were baked at 120°C for 20 min. The active solutions were prepared by blending **P1**:PC₇₁BM in a blend ratio of 1:3(w:w) with a total concentration of 40 mg mL⁻¹ in dichlorobenzene and **P2**:PC₇₁BM in a blend ratio of

1:3 (w:w) with a total concentration of 20 mg mL⁻¹ in chlorobenzene and were stirred overnight in a nitrogen-filled glove box. The active layer was spin-coated onto the PEDOT:PSS layer. **P2**:PC₇₁BM blend films are annealed at 120°C for 20 minutes. Thin layers of Ca (20 nm) and Al (100 nm) were deposited by evaporation through a shadow mask resulting in active device area of 0.045cm².

Inverted devices had an architecture of glass/ITO/ZnO/**P2**:PC₇₁BM/MoO₃/Ag. Indium tin oxide (ITO) patterned glass substrates were cleaned by sonicating in detergent, deionized water, acetone and isopropanol. After oxygen plasma treatment, ZnO layer was deposited by spin coating a zinc acetate dihydrate precursor solution (219.5 mg in the mixture of 2 ml 2-methoxyethanol and 60 μl monoethanolamine) followed by annealing at 150°C for 20 minutes. The active layer blend (ratio of 1:3 (w:w)) was spin-coated from chlorobenzene solution (10 mg/ml with respect to polymer, 2000 r.p.m). Thin layers of MoO₃ (10 nm) and Ag (100 nm) were deposited by evaporation through a shadow mask resulting in active device area of 0.045cm². Current density–voltage (JV) data for the devices were measured using a Xenon lamp at AM1.5 solar illumination (Oriol) calibrated to a silicon reference cell with a Keithley 2400 source meter. EQE was measured by a 100W tungsten halogen lamp (Bentham IL1, Bentham 605 stabilized current power supply) connected to a monochromator and stepper motor.

Differential Scanning Calorimetry

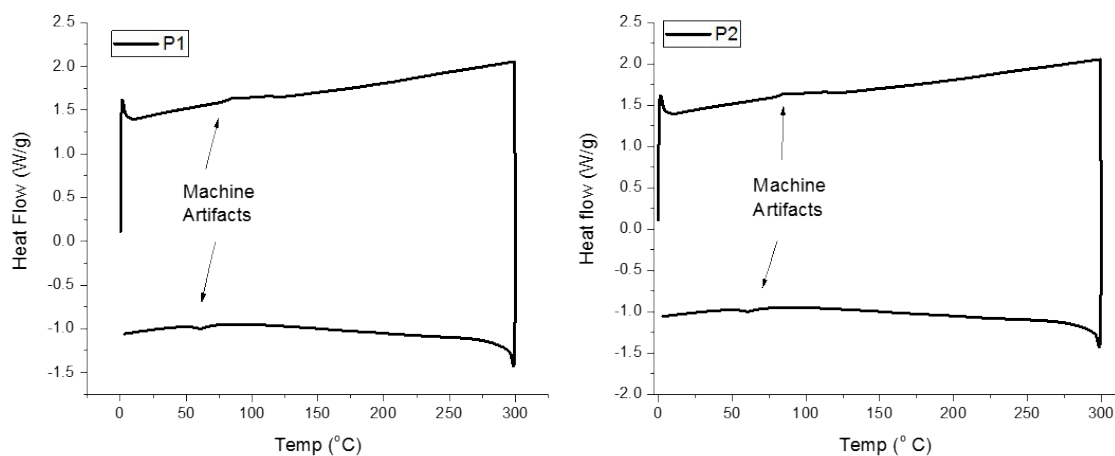


Figure S1. Differential scanning calorimetry traces of P1 and P2 at 10 K/min. Second heating/cooling cycles (endo up)

Cyclic Voltammograms

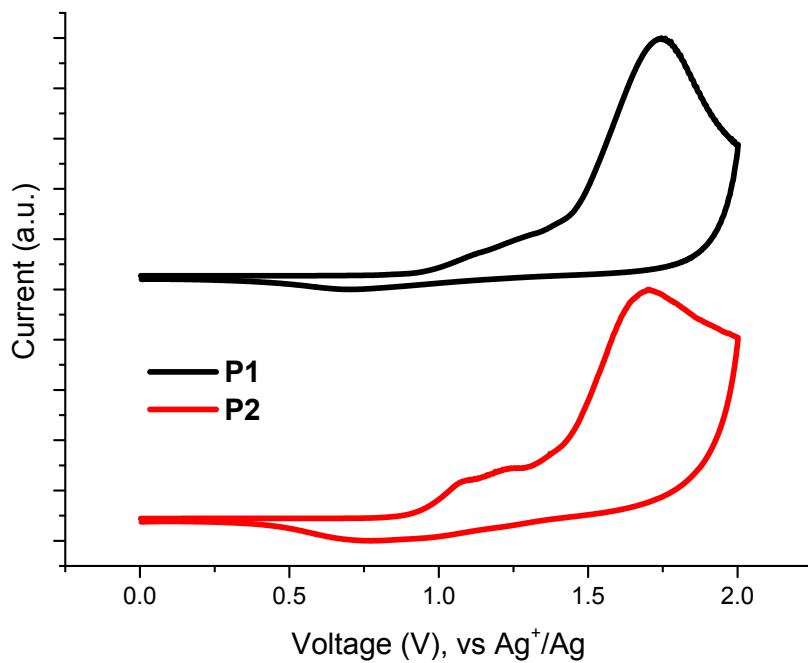


Figure S2: Oxidation cycles of **P1** and **P2**, measured from thin films on fluorine-doped tin oxide (FTO) in 0.1 M Bu₄NPF₆ acetonitrile solutions at a scan rate of 50 mV s⁻¹.

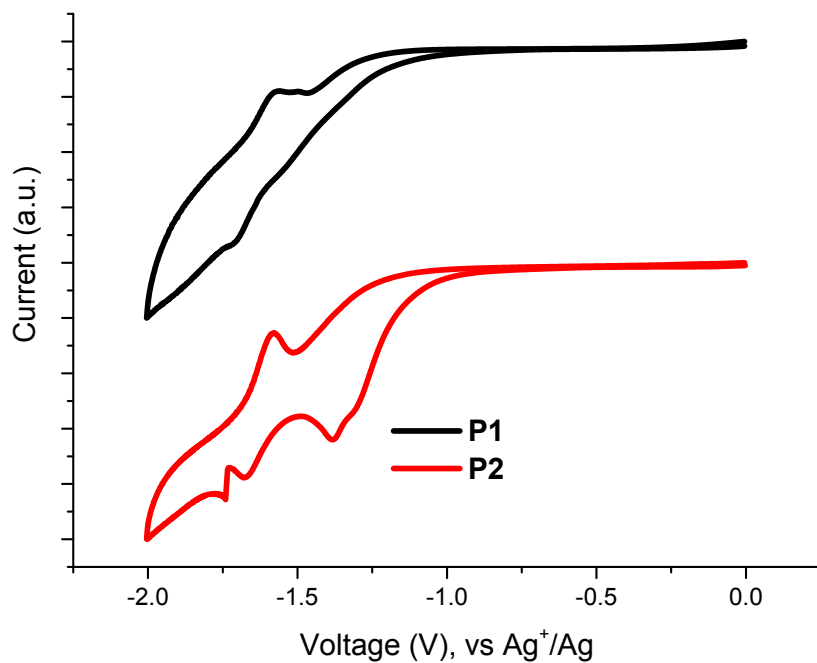


Figure S3: Reduction cycles of **P1** and **P2**, measured from thin films on FTO in 0.1 M Bu₄NPF₆ acetonitrile solutions at a scan rate of 50 mV s⁻¹.

NMR Spectra of Polymers

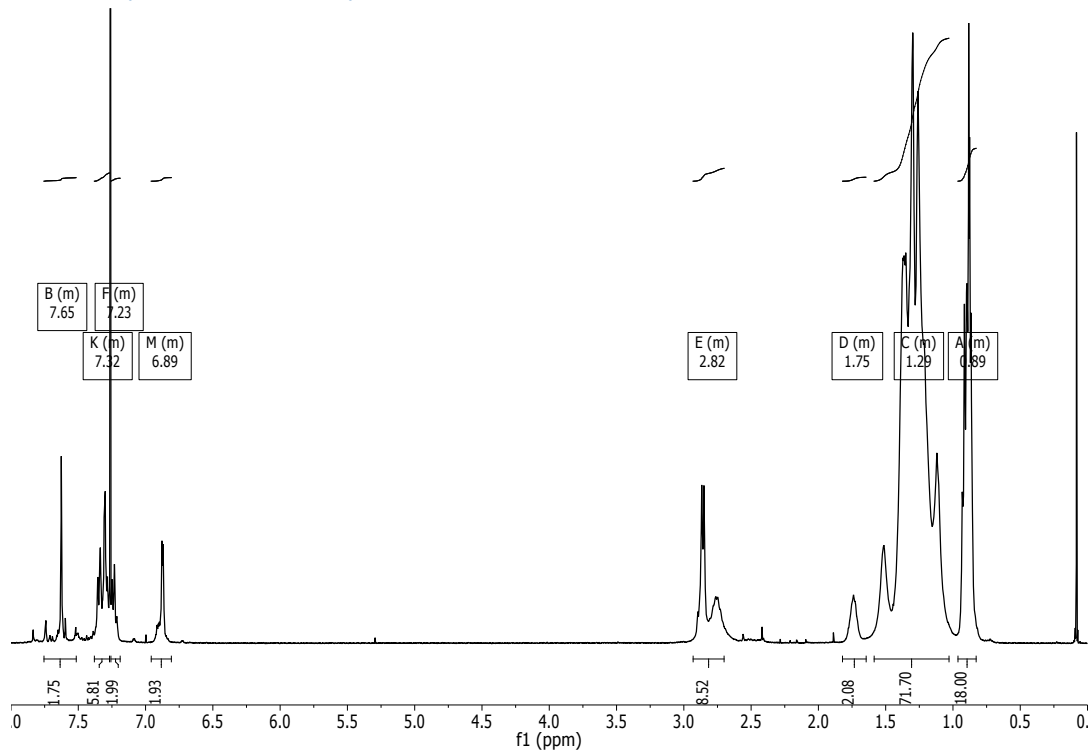


Figure S4: ^1H NMR spectrum of **P1** (400 MHz, 323 K, CDCl_3)

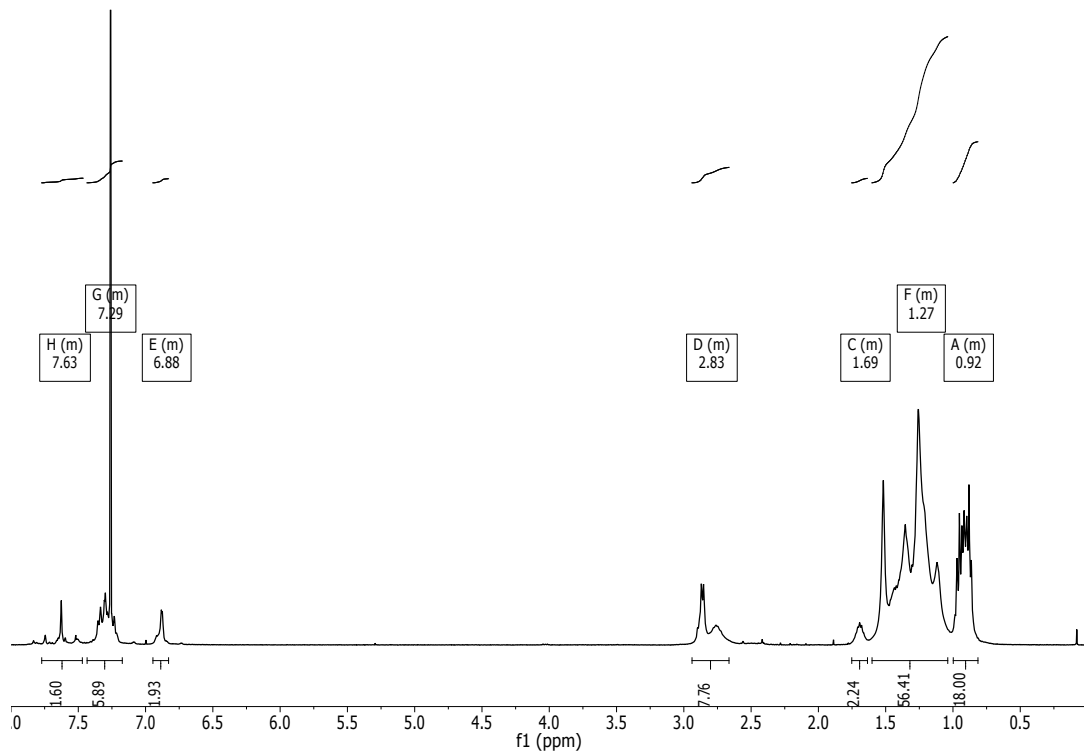


Figure S5: ^1H NMR spectrum of **P2** (400 MHz, 323 K, CDCl_3)

Table S1: Photovoltaic performances of polymers under conditions reported by Park et al. (i.e., optimized for phosphole polymer)

<i>Polymer:PCBM^a</i>	<i>ODT</i>	V_{oc}^{max} (V_{oc}^{avg}) (V)	J_{sc}^{max} (J_{sc}^{avg}) ($mA\ cm^{-2}$)	FF^{max} (FF^{avg})	PCE^{max} (PCE^{avg}) (%)
<i>P1 (1:4)</i>	0.5%	0.82 (0.75±0.05)	5.8 (4.98±0.73)	0.411 (0.37±0.03)	1.97 (1.39±0.36)
<i>P2 (1:4)</i>	0.5%	0.77 (0.78±0.01)	6.7 (5.87±0.68)	0.435 (0.44±0.05)	2.25 (2.02±0.19)

^a average data obtained from four devices. Devices annealed at 120 °C for 20 min after film formation

References

- (1) Green, J. P.; Han, Y.; Kilmurray, R.; McLachlan, M. A.; Anthopoulos, T. D.; Heaney, M. An Air-Stable Semiconducting Polymer Containing Dithieno[3,2-b:2',3'-d]Arsole. *Angew. Chemie Int. Ed.* **2016**, *55* (25), 7148–7151.
- (2) Park, K. H.; Kim, Y. J.; Lee, G. B.; An, T. K.; Park, C. E.; Kwon, S.-K.; Kim, Y.-H. Recently Advanced Polymer Materials Containing Dithieno[3,2-b:2',3'-d]Phosphole Oxide for Efficient Charge Transfer in High-Performance Solar Cells. *Adv. Funct. Mater.* **2015**, *25* (26), 3991–3997.