Supporting Information

Solution Processable Polydiacetylenes (PDAs) through Acyclic Enediyne

Metathesis Polymerization

Keda Hu,^a Haishen Yang,^b Wei Zhang^{*b} and Yang Qin^{*a}

^a Department of Chemistry & Chemical Biology, University of New Mexico, Albuquerque, NM 87131, United States

^b Department of Chemistry & Biochemistry, University of Colorado Boulder, CO 80309, United States

*Corresponding authors. E-mail: wei.zhang@colorado.edu; yangqin@unm.edu

Materials and General Methods. All reagents and solvents were used as received from Sigma-Aldrich or VWR unless otherwise noted. Phenyl-C61-butyric acid methyl ester >99.5%) Dve Source. (PCBM, was purchased from American Triisopropyl((trimethylsilyl)ethynyl)silane was synthesized as described previously.¹ THF was distilled from Na/benzophenone prior to use. Anhydrous dichloromethane was obtained by distillation over CaH₂ and degassed through several freeze-pump-thaw cycles. The 300.13 MHz ¹H and 75.48 MHz ¹³C NMR spectra were recorded on a Bruker Avance III Solution 300 spectrometer. All solution ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks. Size exclusion chromatography (SEC) analyses were performed in chloroform with 0.5% (v/v) triethylamine (1 mL/min) using a Waters Breeze system equipped with a 2707 autosampler, a 1515 isocratic HPLC pump and a 2414 refractive index detector. Two styragel columns (Polymer Laboratories; 5 m Mix-C), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with polystyrene standards (Varian). Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-2401 PC spectrometer over a wavelength range of 250-800 nm. Fluorescence emission spectra were obtained using a Varian Cary Eclipse Fluorometer. Raman spectra were obtained on a DXR SmartRaman spectrometer over a frequency range of 50.5-3350 cm⁻¹. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC STAR^e system with ca. 5 mg sample and at a scan rate of 10 °C / min. The results reported are from the second heating cycle. High resolution mass spectrometry (HRMS) was performed on a Waters/Micromass LCT Premier system operating under electrospray ionization (ESI) mode. Powder X-ray diffraction measurements were performed on a Rigaku SmartLab instrument. Model compound structures were optimized through density functional theory calculations performed on the B3LYP level using 6-31G(d) basis set in the Gaussian 03 Revision C.01 package.²

Solar Cell Fabrication and Testing. ITO-coated glass substrates (China Shenzhen Southern Glass Display. Ltd, 8 Ω/\Box) were cleaned by ultrasonication sequentially in detergent, DI water, acetone and isopropyl alcohol, each for 15 min followed by UV-ozone treatment (PSD Series, Novascan) for 45 min. MoO₃ (10 nm) was deposited inside an glovebox integrated Angstrom Engineering Åmod deposition system at a base vacuum level $< 7 \times 10^{-8}$ Torr. Polymer/PCBM blend solutions were then spun-cast at predetermined speeds using a glovebox integrated spin coater (Special Coating Systems, SCS-G3). Al (100 nm) was lastly thermally evaporated through patterned shadow masks. Current–voltage (I–V) characteristics were measured by a Keithley 2400 source-measuring unit under simulated AM1.5G irradiation (100 mW/cm⁻²) generated by a Xe arc-lamp based Newport 67005 150-W solar simulator equipped with an AM1.5G filter (Newport). The light intensity was calibrated using a Newport thermopile detector (model 818P-010-12) equipped with a Newport 1916-C Optical Power Meter.

1-(Triisopropylsilyl)tetradec-1-yn-3-one (2a). To a suspension of 6.96 g AlCl₃ (52.2 mmol) in 150 mL dry CH₂Cl₂ was added 11.0 g triisopropyl((trimethylsilyl)ethynyl)silane (43.2 mmol) and 10.0 g dodecanoyl chloride 1a (45.7 mmol) at 0 °C. After stirring for 45 min at 0 °C and then 1 h at room temperature, the reaction was quenched with ice water. The reaction mixture was extracted with hexanes twice. The organic layer was combined, washed sequentially with saturated NaHCO₃ solution and brine, and dried over anhydrous Na₂SO₄. Compound **2a** was purified by column chromatography (hexanes as eluent) as a light yellow oil (13.5 g, 85.6%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.87 (t, 3H, J_{HH}^3 = 6.9Hz), 1.09–1.11 (m, 21H), 1.25 (m, 16H), 1.69 (m, 2H,), 2.54 (t, 2H, J_{HH}^3 = 7.2 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 10.9, 14.0, 18.4, 22.6, 24.2, 28.9, 29.3, 29.4, 29.5, 45.5, 95.0, 104.2, 187.7.

(E)-(3,4-Diundecylhexa-3-en-1,5-diyne-1,6-diyl)bis(triisopropylsilane) (3a). To a suspension of 4.84 g zinc powder (74.0 mmol) in 100 mL dry THF was added 4.05 mL TiCl₄ (36.9 mmol) dropwise at 0 °C under nitrogen. The mixture was heated to reflux for 45 min until a dark solution was obtained, and then cooled down to 0 °C. Compound **2a** (8.20 g, 22.5 mmol) was added through a degassed syringe and the reaction mixture was refluxed for an additional 24 h. The reaction was quenched with NaHCO₃, extracted with ethyl ether twice. The combined organic phase was washed with saturated brine and dried over anhydrous Na₂SO₄. Compound **3a** was purified by column chromatography (hexanes as eluent) as a clear oil (5.78 g, 73.7%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.88 (t, 6H, J^3_{HH} = 6.9Hz), 1.08–1.12 (m, 42H), 1.25 (m, 32H), 1.56 (m, 4H), 2.45 (t, 4H, J^3_{HH} = 7.2Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 11.4, 14.1, 18.7, 22.8, 28.4, 29.1, 29.5, 29.6, 29.8, 32.0, 35.2, 100.4, 106.4, 130.6.

(E)-12,13-Diethynyltetracos-12-ene (4a). To a solution of 3a (5.78 g, 8.29 mmol) in 50 mL THF was added 34.4 mL tetrabutylammonium fluoride (1M in THF, 34.4 mmol). The reaction mixture was stirred overnight at room temperature and was extracted with hexanes twice. The combined organic phase was washed with brine solution and dried over Na_2SO_4 . After removal of solvent, the crude product was purified by column chromatography

(hexanes as eluent) to afford **4a** as a white solid (2.89 g, 90.6%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.88 (t, 6H, J^3_{HH} = 6.9 Hz), 1.26 (m, 32H), 1.54 (m, 4H), 2.42 (t, 4H, J^3_{HH} = 7.2 Hz), 3.40 (s, 2H). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 14.1, 22.7, 28.1, 29.0, 29.4, 29.5, 29.6, 29.7, 31.9, 34.8, 82.5, 86.1, 130.3.

(E)-12,13-Di(prop-1-ynyl)tetracos-12-ene (M-a). To a solution of 4a (2.50 g, 6.50 mmol) in 20 mL dry THF was added 6.17 mL ⁿBuLi (2.5M in hexanes, 15.4 mmol) dropwise at -78 °C under nitrogen atmosphere. The mixture was stirred for 15 min and allowed to warm up to room temperature and stirred for additional 15 min. The reaction mixture was then cooled down to -78 °C and 1.2 mL CH₃I (19.3 mmol) was added through a syringe. The solution was slowly warmed up to room temperature and stirred for another 2 h. The reaction mixture was quenched with water and extracted with hexanes twice. The combined organic phase was washed with brine solution and dried over Na₂SO₄. After removal of solvent the crude product was purified by column chromatography (hexanes as eluent) and recrystallized from hexanes to give **M-a** as a white solid (2.4 g, 89.5%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.88 (t, 6H, J^3_{HH} = 6.9 Hz), 1.26 (m, 32H), 1.50 (m, 4H), 2.02 (s, 6H), 2.34 (t, 4H, J^3_{HH} = 7.2Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm)=4.7, 14.1, 22.7, 28.4, 29.0, 29.4, 29.5, 29.6, 29.7, 31.9, 34.9, 79.2, 93.6, 128.6. HRMS (m/z): *calc.* for C₂₈H₃₂: 369.2582 [M+H]⁺, 391.2402 [M+Na]⁺; found: 369.2577 [M+H]⁺, 391.2522 [M+Na]⁺.

PDA-CH. The ligand L (15 mg, 0.036 mmol) and the catalyst precursor Mo (24 mg, 0.036 mmol) were premixed in dry CCl₄ (4 mL) for 10 minutes at r.t. to generate the active catalyst in situ. Subsequently, the monomer (**M-a**) (200 mg, 0.48 mmol) was added together with 5 Å molecular sieves (1.8 g, powder) with the aid of CCl₄ (8 mL). The resultant suspension was stirred at 60 °C for 3 d. Then the solids in the reaction mixture were separated by centrifugation, followed by washing with CHCl₃ (4 × 12 mL). The combined solution was filtered through a pad of celite. The filtrate was concentrated to ca. 10 mL, and methanol (ca. 60 mL) was added. The red precipitates were collected by filtration, washed with methanol (ca. 15 mL) and dried under high vacuum (155 mg, 90%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.84-0.90, 1.26, 1.54-1.59, 2.48. ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 14.1, 21.5, 22.7, 27.7, 28.8, 29.8, 31.9, 35.4, 45.2, 99.3, 129.8. SEC (CHCl₃, 1 mL/min): $M_n = 15,600, M_w = 29,640, PDI = 1.9$.

1-(4-Tert-butylphenyl)-3-(triisopropylsilyl)prop-2-yn-1-one (2b). The compound **2b** was prepared from **1b** according to the procedures described for the synthesis of 2a. (84.3%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 1.15–1.19 (m, 21H), 1.35 (s, 9H), 7.51 (d, 2H, J^{3}_{HH} = 8.4Hz), 8.11 (d, 2H, J^{3}_{HH} = 8.4Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 11.1, 18.6, 31.0, 35.2, 97.2, 103.2, 125.6, 129.5, 134.3, 158.0, 177.1.

(E)-(3,4-bis(4-tert-butylphenyl)hexa-3-en-1,5-diyne-1,6-diyl) bis(triisopropylsilane) (3b). The compound 3b was prepared from 2b according to the procedures described for the synthesis of 3a. (73.1%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 0.99–1.11 (m, 42H), 1.32 (s, 18H), 7.33 (d, 4H, J^{3}_{HH} = 8.7Hz), 7.80 (d, 4H, J^{3}_{HH} = 8.7Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 11.3, 18.6, 31.3, 34.6, 101.2, 107.5, 124.6, 129.0, 129.2, 136.1, 150.9. ((E)-4,4'-(hexa-3-en-1,5-diyne-3,4-diyl)bis(tert-butylbenzene) (4b). The compound 4b was prepared from 3b according to the procedures described for the synthesis of 4a. (Yield 75.5%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 1.34 (s, 18H), 3.40 (s, 2H), 7.41 (d, 4H, J^{3}_{HH} = 8.7Hz), 7.79 (d, 4H, J^{3}_{HH} = 8.7Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 31.3, 34.7, 84.0, 86.7, 124.8, 128.4, 128.7, 135.4, 151.5.

(E)-4,4'-(octa-4-en-2,6-diyne-4,5-diyl)bis(tert-butylbenzene) (M-b). The monomer M-b was prepared from 4b according to the procedures described for the synthesis of M-a as a slightly yellow solid. (88.2%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 1.34 (s, 18H), 1.96 (s, 6H), 7.38 (d, 4H, J^{3}_{HH} = 8.7Hz), 7.79 (d, 4H, J^{3}_{HH} = 8.7Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) = 5.0, 31.3, 34.6, 81.0, 94.5, 124.6, 127.1, 128.6, 136.9, 150.6. HRMS (m/z): *calc.* for C₃₀H₅₂: 412.4069 [M]⁺, 413.4147 [M+H]⁺; found: 412.4079 [M]⁺, 413.4149 [M+H]⁺.

PDA-Ph. The ligand L (11 mg, 0.026 mmol) and the catalyst precursor Mo (17 mg, 0.026 mmol) were premixed in dry CCl₄ (3 mL) for 10 minutes at r.t. to generate the active catalyst *in situ*. Subsequently, the monomer M-b (127 mg, 0.34 mmol) was added together with 5 Å molecular sieves (1.3 g, powder) with the aid of CCl₄ (5 mL). The resultant suspension was stirred at 60 °C for 3 d. Then the molecular sieves were removed by filtration and the filtrate was concentrated under vacuum. The obtained residue was dissolved in ethyl ether (ca. 20 mL), followed by the addition of methanol (ca. 20 mL). The red precipitate was collected and dried under high vacuum overnight (87 mg, 80%). ¹H NMR (300.13 MHz, CDCl₃): δ (ppm) = 1.23-1.28, 7.09-7.11, 7.36-7.38. ¹³C NMR (75.48 MHz, CDCl₃), δ (ppm) =31.4, 34.6, 99.9, 124.5, 128.3, 128.9, 135.4, 150.8. SEC (CHCl₃, 1 mL/min): $M_n = 10,200$, $M_w = 14,280$, *PDI* = 1.4.

Reference:

- 1. Helal, C. J.; Magriotis, P. A.; Corey, E. J. J. Am. Chem. Soc. 1996, 118, 10938.
- Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004..



Figure S1. Size exclusion chromatograms of **PDA-CH** and **PDA-Ph** (CHCl₃ w/ 0.5% NEt₃, 1 mL/min, RI detector).



Figure S2. UV-Vis absorption spectra of chloroform (black) and mixtures of chloroform and methanol (red: 17% methanol; blue: 29% methanol; by volume).



Figure S3. UV-Vis absorption spectra of PDA-CH and PDA-Ph in THF at various temperatures.



Figure S4. Density functional theory (DFT) calculations (B3LYP, 6-31G(d)) on polydiacetylene (PDA) model compounds having three repeating units bearing methyl (TriDA-Me) and phenyl (TriDA-Ph) substituents.



Figure S5. Differential scanning calorimetry (DSC) histograms of **PDA-CH** and **PDA-Ph**; 2nd heating curves, 10 °C/min.



Figure S6. Powder X-ray diffraction pattern of PDA-CH.



Figure S7. Powder X-ray diffraction pattern of PDA-Ph.



Figure S8. UV-Vis absorption spectra of PDA-CH and PDA-Ph thin films drop cast from chloroform solutions at various temperatures.



Figure S9. Current-voltage curves of solar cells based on 1:1 (wt:wt) PCBM blends of respective **PDA-CH** and **PDA-Ph** in dark and under simulated AM 1.5G solar irradiation (100 mW/cm²).





















Electronic Supplementary Material (ESI) for Chemical Science This journal is O The Royal Society of Chemistry 2013



Electronic Supplementary Material (ESI) for Chemical Science This journal is The Royal Society of Chemistry 2013

