Supplementary Information

A promising combination of brand-new silole-containing ladder-type heptacylic arene and naphthobisoxadiazole moieties for highly efficient polymer solar cells

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Experimental Section

Measurement and Characterization: All NMR spectra were obtained on a Varian Mercury 400 in deuterated chloroform solution with 0.003%TMS as internal reference. Mass spectra were obtained on a FINNIGAN LCQ mass spectrometer. Chemical shift (δ) were reported in parts per million (ppm), and coupling constant (J) were recorded in Hertz (Hz). Molecular weight and molecular weight distribution were analyzed by a Waters GPC (Breeze system) using tetrahydrofuran (THF) as an eluent at 35 °C. The apparatus was equipped with two Waters Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414), and a dual-wavelength absorbance detector (Waters 2487). Polystyrene standards (Waters) were used for calibration. The polymer film was coated on ITO sheets by solvent casting. Cyclic voltammetry (CV) was conducted on an Autolab PGSTAT 30 Electrochemical Workstation with Ag, Ag/Ag⁺, Pt wire as working electrode, reference electrode, and counter electrode,

respectively, in a solution of 0.1 M tetrabutylammonium perchlorate (Bu4NCl6) in deoxygenated acetonitrile (CH₃CN) at a scan rate of 50 mV s⁻¹. The potential of the polymer was corrected in the standard of Fc/Fc⁺ in CH₃CN (0.45 V vs. Ag/Ag⁺ electrode). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at heating rates of 10 and 5 °C min⁻¹ using a TA Instruments (TGA-951 and DSC-910S, respectively). Tapping mode atom force microscopy (TM-AFM) images were taken on a NanoScope IIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA), using built-in software (version V6.13R1) to capture images. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at the BL23A1 endstation of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The thin films for characterization were deposited on a 1 cm \times 2 cm silicon wafer. A monochromatic beam of wavelength $\lambda = 0.826$ Å (15 keV) was used and the incident angle was 0.2°. The scattering patterns were collected on a CMOS flat panel X-ray detector C9728DK (52.8 mm \times 52.8 mm). The scattering intensity profiles were extracted from the 2D patterns and reported as the plots of the scattering intensity I vs. the scattering vector q, where $q = (4\pi/\lambda) \sin(\theta/2)$ and θ is the scattering angle. The absorption spectra were obtained on a Hitachi U-4100 spectrophotometer. Hole-only devices were fabricated according to a similar method described in the literature,^[1] using a diode configuration of ITO/PEDOT:PSS/polymer/Pd (50 nm). The SCLC current was measured under dark conditions using a Keithley 2400 Source Meter.

Solar Cell Device Fabrication and Characterization: The conventional PSCs were fabricated with the device structure of ITO/PEDOT:PSS (40 nm)/polymer:PC₇₁BM (90-115 nm)/poly[(9,9-dioctyl-2,7-fluorene)-alt-(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)] (PFN) (5 nm)/Ca (20nm)/Al (100nm). Prior to use, patterned ITO-coated glass substrates (15 Ω /square) were successively cleaned by ultrasonication in 1% neutral detergent in water, then

deionized water, followed by acetone and finally isopropanol for 10 min each and subsequently dried under a stream of dry nitrogen. The substrates were then underwent oxygen plasma treatment for 20 min prior to the deposition of a ~40-nm-thick layer of PEDOT:PSS, as verified by a Filmetrics Model F10-RT-UV system. Deposition of the PEDOT:PSS layer was followed by baking at 150 °C for 15 min in air and then transferred into an inert N₂-filled glove box (< 0.1 ppm O₂ and H₂O) for subsequent procedures. Blend solutions were prepared by dissolving the target polymer (PSiNO or PSiBO) and PC71BM (purchased from Nano-C) in o-DCB solution in blend ratios of 1:1, 1:1.5 and 1:2 with a polymer concentration of 10 mg mL⁻¹ and were heated to 100 °C and stirred 8 h for complete dissolution. Then the blend solution was spin-casted after adding 0.5% and 3% (v/v) DIO for PSiNO and PSiBO-based systems. The wet film was slowly dried in a covered Petri dish for 30 min in the glove box. Afterwards, methanol was dropped onto the active layer with a spincasting rate at 2000 rpm for 60 s, and subsequently PFN interfacial layer was spin-casted onto the active layer according to a similar method described in the literature.^[2] The coated substrates were then transferred to a thermal evaporator and evacuated to $\leq 5 \times 10^{-6}$ Torr before a 20-nm-thick calcium layer followed by a 100-nm aluminium electrode layer were deposited. The effective area of one cell was 0.04 cm². The fabricated device was encapsulated in a nitrogen-filled glove box with UV epoxy and cover glass. The inverted PSCs were fabricated with the configuration of ITO/ZnO (40 nm)/PFN (5 nm)/PSiNO:PC71BM (~110 nm)/MoO3 (8 nm)/Ag (100 nm). Molybdenum oxide was thermally deposited on top of the active layer with an evaporation rate of 0.1 Å s⁻¹ under a vacuum $\leq 5 \times 10^{-6}$ Torr. Ultimately, 100 nm silver film was deposited on top of the molybdenum oxide layer through a shade mask. The J-V curves were measured with a Newport-Oriel (Sol3A Class AAA Solar Simulators) AM 1.5G light source operating at 100 mW cm⁻², and independently cross-checked using a 300 W AM 1.5G source operating at 100 mW cm⁻² for verification. The light intensity was determined by a monosilicon detector (with

KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL) to minimize spectral mismatch. An IPCE (QE10) characterization platform supplied by PV Measurement, Inc. was used for data acquisition. All IPCE spectra were recorded using a lock-in technique at a chopping frequency of 100 Hz.

Synthetic Procedures: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere.

Synthesis of 2,3,6,7-tetrabromo-4,8-dihexylbenzo[1,2-b:4,5-b']dithiophene (2): 4,8-Dihexylbenzo[1,2-b:4,5-b']dithiophene (1, 8.61 g, 24 mmol) was dissolved in a mixed solvent of chloroform (240 mL) and acetic acid (120 mL). Bromine (2.47 mL, 48 mmol) was added dropwise into the reaction mixture through an addition funnel under absence of light, and then stirred for 1h at room temperature. More bromine (3.71 mL, 72 mmol) was then added, and the reactant was heated to 80 °C for overnight after the addition. After cooling to room temperature, the reactant was poured into a mixture of ice and saturated NaOH aqueous solution, followed by extraction with water and CH₂Cl₂. The combined extracts was washed with brine, dried over anhydrous MgSO₄, and then filtrated. The solvent was removed by rotary evaporation, and the crude product was washed with methanol to afford 2 as a pale yellow solid (13.53 g, 84 %). ¹H NMR (CDCl₃, 400 MHz) δ 3.39 (t, J = 8.4 Hz, 4H), 1.76-1.68 (m, 4H), 1.53-1.47 (m, 4H), 1.37-1.34 (m, 8H), 0.91 (t, J = 6.8 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) & 138.9, 130.0, 129.2, 116.8, 109.1, 31,6, 31.2, 31.0, 29.6, 14.2; HRMS (*m/z*, FAB⁺) Calcd for C₂₂H₂₆⁷⁹Br₄S₂ 669.8209, found 669.8207; calcd for C₂₂H₂₆⁷⁹Br₃⁸¹BrS₂ 671.8189, found 671.8192; calcd for C₂₂H₂₆⁷⁹Br₂⁸¹Br₂S₂ 673.8168, found 673.8164; calcd for C22H26⁷⁹Br⁸¹Br₃S₂ 675.8148, found 675.8157; calcd for C22H26⁸¹Br₄S₂ 677.8128, found 677.8126.

of 3,7-dibromo-2,6-bis(3-bromothiophen-2-yl)4,8-dihexylbenzo[1,2-b:4,5-b'] *Svnthesis* dithiophene (3): To a flame-dried three neck flask was added 2,3-dibromothiophene (14.52 g, 60 mmol) and anhydrous ether (60 mL) under argon atmosphere. The solution was cooled to -78 °C, before *n*-BuLi (1.6 M in hexane, 37.50 mL, 60 mmol) was added dropwise. After the addition was completed, the reactant was stirred at -78 °C for 1h, and an 0.5 M THF solution of ZnCl₂ (120 mL, 60 mmol) was added quickly. The reactant was then stirred at 0 °C for 1h, and transferred through cannula into a two neck flask containing a solution of 2 (13.48 g, 20 mmol) and Pd(PPh₃)₄ (1.85 g, 1.6 mmol) in anhydrous THF (120 mL). After heated to reflux for 4 days, the reactant was cooled to room temperature and quenched with saturated NH₄Cl aqueous solution (200 mL), followed by extraction with water and ether. The combined extracts was washed with brine, dried over anhydrous MgSO₄, and then filtrated. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with hexane as eluent to afford **3** as a bright yellow solid (8.65 g, 52 %). ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, *J* = 5.6 Hz, 2H), 7.14 (d, *J* = 5.6 Hz, 2H), 3.60 (t, J = 8.4 Hz, 4H), 1.90-1.82 (m, 4H), 1.59-1.52 (m, 4H), 1.43-1.33 (m, 8H), 0.91 (t, J = 6.8 Hz, 41)Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 139.3, 130.9, 130.8, 130,7, 129.9, 128.2, 113.5, 108.6, 31.6, 31.4, 31.0, 29.7, 22.8, 14.2; HRMS $(m/z, \text{ESI}, [M+Na]^+)$ Calcd for C₃₀H₃₀⁷⁹Br₄S₄Na 856.7862, found 856.7847; calcd for C₃₀H₃₀⁷⁹Br₃⁸¹BrS₄Na 858.7841, found 858.7828; calcd for C₃₀H₃₀⁷⁹Br₂⁸¹Br₂S₄Na 860.7821, found 860.7814; calcd for C₃₀H₃₀⁷⁹Br⁸¹Br₃S₄Na 862.7800, found 862.7787; calcd for C₃₀H₃₀⁸¹Br₄S₄Na 864.7780, found 864.7771.

Synthesis of 3,7-dibromo-2,6-bis(4-bromo-2-trimethylsilylthiophen-5-yl)4,8-dihexylbenzo [1,2-b:4,5-b']dithiophene (4): To a solution of diisopropylamine (2.99 mL, 21.3 mmol) in anhydrous THF (10.65 mL) was added *n*-BuLi (1.6 M in hexane, 13.31 mL, 21.3 mmol) dropwise at 0 °C under argon atmosphere. After being stirred at 0 °C for 30 minutes, the ice

bath was removed and the reactant was warmed to room temperature followed by stirring for an additional 30 minutes. The freshly made lithium diisopropylamide solution was then transferred into an addition funnel which was attached onto a two neck bottle containing a solution of 3 (6.88 g, 8.20 mmol) in anhydrous THF (246 mL) before it was added dropwise into the solution at -60 °C. The reactant was stirred at same temperature for 30 minutes, 30 minutes at 0 °C, and then cooled down to -60 °C again before the addition of trimethylchlorosilane (3.12 mL, 24.6 mmol). After the addition, the reactant was stirred overnight and slowly warmed to room temperature, quenched with water and extracted with ether. The combined extracts was washed with brine, dried over anhydrous MgSO₄, and then filtrated. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with hexane as eluent to afford 4 as a bright yellow solid (7.03 g, 89 %). ¹H NMR (CDCl₃, 400 MHz) δ 7.21 (s, 2H), 3.59 (t, J = 8.4 Hz, 4H), 1.88-1.84 (m, 4H), 1.56-1.53 (m, 4H), 1.41-1.34 (m, 8H), 0.91 (t, J = 6.8 Hz, 6H), 0.39 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.1, 139.2, 136.8, 134.6, 131.1, 130.9, 130.7, 114.3, 108.0, 31.7, 31.5, 31.0, 29.8, 22.8, 14.3, -0.2; HRMS (m/z, ESI, [M+Na]⁺) Calcd for C₃₆H₄₆⁷⁹Br₄S₄Si₂Na 1000.8652, found 1000.8654; calcd for C₃₆H₄₆⁷⁹Br₃⁸¹BrS₄Si₂Na 1002.8632, found 1002.8639; calcd for $C_{36}H_{46}^{79}Br_2^{81}Br_2S_4Si_2Na$ 1004.8611, found 1004.8623; calcd for C36H4679Br81Br 3S4Si2Na 1006.8591, found 1006.8597; calcd for C36H4681Br 4S4Si2Na 1008.8570, found 1008.8573.

Synthesis of 5,11-dihexyl-4,4,10,10-tetraoctyl-2,8-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bisthieno[4",5"-b":4"',5"'-b"']silolo[2",3"-d:2"',3"'-d']thiophene (TMS-ARSi, 5): To 4 (3.93 g, 4.0 mmol) in anhydrous THF (120 mL) was added t-BuLi (1.64 M in pentane, 20.00 mL, 32.4 mmol) at -90 °C under argon atmosphere and then stirred for 2h. A solution of dichlorodioctylsilane (3.60 mL, 10.4 mmol) in anhydrous THF (10.40 mL) was added dropwise into the reaction mixture at low temperature, then the reactant was allowed to slowly warm to room temperature overnight while maintaining stirring. The reactant was quenched by addition of water, and extracted with hexane. The combined extracts was washed with brine, dried over anhydrous MgSO₄, and then filtrated. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with hexane as eluent to afford **5** as a sticky orange liquid (3.13 g, 67 %). ¹H NMR (CDCl₃, 400 MHz) δ 7.22 (s, 2H), 3.13 (t, *J* = 8.4 Hz, 4H), 1.84 (m, 4H), 1.61-1.57 (m, 4H), 1.43-1.12 (m, 64H), 0.97 (t, *J* = 6.8 Hz, 6H), 0.87 (t, *J* = 6.8 Hz, 12H), 0.40 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.5, 148.6, 143.7, 142.4, 141.5, 138.4, 136.5, 134.7, 129.5, 35.8, 33.3, 32.0, 31.9, 30.4, 29.6, 29.3, 29.2, 24.3, 22.9, 22.8, 14.3, 14.2, 13.1, 0.4; HRMS (*m*/*z*, ESI, [M+Na]⁺) Calcd for C₆₈H₁₁₄S₄Si₄Na 1193.6778, found 1198.6769.

Synthesis of 2,8-dibromo-5,11-dihexyl-4,4,10,10-tetraoctylbenzo[1,2-b:4,5-b']bis-thieno [4",5"-b":4"",5""-b"]silolo[2",3"-d:2"",3""-d']thiophene (Br-ARSi, 6): A solution of Nbromosuccinimide (934 mg, 5.25 mmol) in anhydrous THF (100 mL) was added dropwise into a solution of **5** (2.93 g, 2.50 mmol) in anhydrous THF (100 mL) at 0 °C with the absence of light. The reactant was stirred overnight and slowly warmed to room temperature, followed by extraction with water and hexane. The combined extracts was washed with brine, dried over anhydrous MgSO4, and then filtrated. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with hexane as eluent to afford **6** as a sticky orange liquid (2.16 g, 73 %). ¹H NMR (CDCl₃, 400 MHz) δ 7.09 (s, 2H), 3.08 (t, *J* = 8.4 Hz, 4H), 1.81-1.78 (m, 4H), 1.58 (m, 4H), 1.40-1.09 (m, 64H), 0.95 (t, *J* = 6.8 Hz, 6H), 0.83 (t, *J* = 6.8 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.8, 148.2, 142.7, 141.6, 138.3, 133.6, 132.5, 129.7, 112.5, 35.7, 33.2, 31.9, 31.8, 30.3, 29.5, 29.2, 29.0, 24.1, 22.8, 22.6, 14.1, 14.0, 12.7; HRMS *m*/z, ESI, [M+Na]⁺) Calcd for C₆₂H₉₆⁷⁹Br₂S4Si₂Na 1205.4198, found 1205.4179; calcd for C₆₂H₉₆⁷⁹Br⁸¹BrS4Si₂Na 1207.4177, found 1205.4125; clacd for C₆₂H₉₆⁸¹Br₂S₄Si₂Na 1209.4157, found 1209.4110.

Synthesis of 5,11-dihexyl-4,4,10,10-tetraoctyl-2,8-bis(trimethylstannyl)benzo[1,2-b:4,5-b']bis-thieno[4",5"-b":4"',5"'-b"']silolo[2",3"-d:2"',3"'-d']thiophene (Sn-ARSi, 7): A solution of **6** (783 mg, 0.66 mmol) in anhydrous THF (66 mL) was added dropwise *t*-BuLi (1.64 M in pentane, 1.69 mL, 2.77 mmol) at -90 °C under argon atmosphere and then stirred for 1h. Trimethyltin chloride solution (1 M in hexane, 2.90 mL, 2.90 mmol) was subsequently added in one portion into the reaction mixture. The reactant was stirred overnight and slowly warmed to room temperature, quenched with water and extracted with hexane. The combined extracts was washed with brine, dried over anhydrous MgSO4, and then filtrated. The solvent was removed by rotary evaporation to afford **7** as sticky orange oil and used without further purifications (812 mg, 91 %).

Synthesis of 4,7-Dibromobenzo[c][1,2,5]oxadiazole (DiBr-BO): This compound was prepared according to the literature procedure.^{[3] 1}H NMR (CDCl₃, 400 MHz) δ 7.49 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.4, 134.2, 180.7.

Synthesis of Naphtho[1,2-*c*:5,6-*c'*]-*bis*[1,2,5]*oxadiazole (NO):* 5% Sodium hypochlorite solution (21 mL) was dropwise added to a stirred, cooled solution of 1,5-dinitronaphthalene-2,6-diamine (2.0 g, 6.4 mmol) in 1 M alcoholic sodium hydroxide (300 mL) at 0 °C. The mixture was stirred at this temperature for an additional 30 min. Then, most ethanol was removed under reduced pressure, and the residue was filtered and washed with sufficient amount of water to afford **NO**'s dioxide as dark yellow solid. The **NO**'s dioxide could be used in the following reaction without further purification and drying. A mixture of **NO**'s dioxide, PPh₃ (4.8 g, 18.3 mmol) and THF (20 mL) was charged under nitrogen and stirred at 80 °C for 30 h until the starting material is consumed (TLC). After cooling to room temperature, the

solution was removed under reduced pressure, and the residue was dissolved in CH₂Cl₂, washed with water, dried over MgSO₄, concentrated to give a crude product. The residue was washed with ethanol to give the pure compound (0.58 g, 43 %). ¹H NMR (CDCl₃, 400 MHz) δ 8.51 (d, *J* = 9.2 Hz, 2H), 8.07 (d, *J* = 9.2Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 148.9, 147.5, 128.7, 122.9, 117.4; HRMS (*m/z*, FAB⁺) Calcd for C₁₀H₄N₄O₂ 212.0334, found 212.0332.

Synthesis of 4,9-dibromonaphtho[1,2-c:5,6-c']-bis[1,2,5]oxadiazole (DiBr-NO): Compound **NO** (0.37 g, 1.75 mmol) and NBS (0.93 g, 5.23 mmol) were dissolved in a mixed solvent of sulfuric acid (7 mL) and trifluoroacetic acid (21 mL). The solution was stirred at room temperature overnight. Then the mixture was poured into ice water carefully, and the crude product was precipitated and collected by filtration. The residue was washed with water, ethanol and chloroform to give the pure compounds (0.31 g, 48 %). ¹H NMR (CDCl₃, 400 MHz) δ 8.67(s, 2H). ¹³C NMR could not be recorded due to the low solubility of **DiBr-NO**. HRMS (*m/z*, FAB⁺) Calcd for C₁₀H₂⁷⁹Br₂N₄O₂ 367.8545, found 367.8549; calcd for C₁₀H₂⁷⁹Br⁸¹BrN₄O₂ 369.8524, found 369.8530; clacd for C₁₀H₂⁸¹Br₂N₄O₂ 371.8504, found 371.8512.

General procedures of polymerization: Ditin-monomer (0.3 mmol), dibromo-monomer (0.3 mmol), tri(*o*-tolyl)phosphine (16 mol% with respect to the ditin-monomer), and tris(dibenzylideneacetone)dipalladium(0) (2 mol% with respect to the ditin-monomer) were dissolved in degassed chlorobenzene (5 mL). Then, the copolymer was synthesized *via* microwave-assisted Stille polycondensation (150 °C for 30 min). After end-capping with trimethyl(thiophen-2-yl)stannane and 2-bromothiophene (both 1.1 equiv. with respect to the mixture was

cooled and poured into methanol to afford a solid precipitate. The crude polymer was extracted using the Soxhlet apparatus with methanol, acetone, hexane, CH_2Cl_2 , and chloroform. The polymers extracted from solvents were precipitated in methanol and dried overnight under vacuum at 60 °C.

PSiBO. Compound **DiBr-BO** was selected as the dibromo-monomer for polymerization. Hexane extracted most of polymer in the Soxhlet apparatus to give **PSiBO** as brown solid (315 mg, 92 %). GPC: $M_n = 61.8$ kDa, $M_w = 172.8$ kDa, PDI = 2.8. ¹H NMR (*d*₂-1,1,2,2-tetrachloroethane, 400 MHz) δ 8.71 (s, 2H), 7.75 (s, 2H), 2.28-0.74 (bm, 94H).

PSiNO. Compound **DiBr-NO** was selected as the dibromo-monomer for polymerization of **PSiNO**. Chloroform extracted most of polymer in the Soxhlet apparatus (203 mg, 48 %). GPC: $M_n = 100.4$ kDa, $M_w = 151.4$ kDa, PDI = 1.5. ¹H NMR (400 MHz, *d*₂-1,1,2,2-tetrachloroethane, ppm): $\delta = 8.07$ (bm, 4H), 3.17-0.66 (bm, 94H).



Fig. S1 Single-crystal X-ray structures of dibromo-ARSi (6) and NO. Hydrogen atoms are removed for clarity.



Fig. S2 Crystal packing diagram of dibromo-ARSi (6).



Fig. S3 a) Thermogravimetric analysis (ramp rate: 10 °C min⁻¹) of PSiNO and PSiBO copolymers. The purge gas for TGA was nitrogen. The onset decomposition temperatures of PSiNO and PSiBO at 5% weight loss are 386 and 383 °C, respectively. b) DSC curve of the studied copolymers.



Fig. S4 Minimum energy conformations of tetramers of PSiNO and PSiBO. Gaussian optimized at B3LYP/6-31G* level with visualization of the corresponding HOMO/LUMO energy distributions.



Fig. S5 Cyclic voltammograms of the polymer films on platinum electrode in 0.1 mol L^{-1} Bu4NPF6 acetonitrile solution at a scan rate of 50 mV s⁻¹.



Fig. S6 Determination of the hole mobility from the dark current densities for the pristine PSiNO and PSiBO polymers.



Fig. S7 Current density versus voltage (*J*–*V*) characteristics of optimized devices made from various blend ratios of a) PSiNO:PC71BM with 0.5% 1,8-diiodooctane (DIO) adopted as an additive and b) PSiBO:PC71BM with 3% DIO under AM1.5 white light illumination at 100 mW cm⁻².



Fig. S8 UV-vis spectra of a) PSiNO:PC71BM and b) PSiBO:PC71BM blend films.



Fig. S9 Schematic illustration of alkyl side-chains interdigitating and/or tilting out of the a) PSiBO and b) PSiNO polymer backbone plane in the solid state.



Fig. S10 ¹H NMR spectra of two polymers PSiBO and PSiNO.



S16





Fig. S13 ¹H NMR and ¹³C NMR spectra of compound 4.



S19





Fig. S16 ¹H NMR and ¹³C NMR spectra of NO.



	6	NO		
CCDC NO.	1014680	1013475		
Empirical formula	C62H96Br2S4Si2	C10 H4 N4 O2		
Formula weight	1185.63	212.17		
Temperature	295(2) K	150(2) K		
Wavelength	1.54178 Å	0.71073 Å		
Crystal system	Triclicnic	Monoclinic		
Space group	P1	P2(1)/n		
	$a = 9.6261(4) \text{ Å} \alpha = 92.491(5)^{\circ}$	$a = 3.7449(3) \text{ Å} \ \alpha = 90^{\circ}$		
Unit cell dimensions	$b = 10.7307(6) \text{ Å} \beta = 98.119(5)^{\circ}$	$b = 6.5953(5) \text{ Å} \beta = 93.931(2)^{\circ}$		
	$c = 17.4242(11) \text{ Å} \gamma = 108.490(5)^{\circ}$	$c = 17.3411(14) \text{ Å} \gamma = 90^{\circ}$		
Volume	168.33(16) Å ³	427.30(6) Å ³		
Ζ	1	2		
Density (calculated)	1.170 mg/m ³	1.649 mg/m ³		
Absorption coefficient	3.273 mm ⁻¹	0.122 mm ⁻¹		
F(000)	630	216		
Crystal size	0.20 x 0.10 x 0.10 mm ³	0.50 x 0.25 x 0.08 mm ³		
Theta range for data collection	4.36 to 67.99°	2.35 to 27.48°		
In day, non and	-11<=h<=9,	-4<=h<=4,		
Index ranges	-11<=k<=12, -20<=l<=20	-8<=k<=8, -22<=1<=22		
Reflections collected	14644	3681		
Independent reflections	7675 [R(int) = 0.0316]	974 [R(int) = 0.0312]		
S22				

Table S1	Crystal	data	and	structure	refinement	for	compound	s 6	and	N()
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Completeness to theta = 27.50°	99.8 %	100.0 %
Absorption correction	None	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.86597	0.9903 and 0.9415
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7675 / 477/ 538	974 / 0 / 73
Goodness-of-fit on F ²	1.133	1.122
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1696	R1 = 0.0473, $wR2 = 0.1220$
R indices (all data)	R1 = 0.1101, $wR2 = 0.2140$	R1 = 0.0552, $wR2 = 0.1289$
Largest diff. peak and hole	0.484 and -0.285 e.Å ⁻³	0.269 and -0.256 e.Å ⁻³

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