

Supporting Information

Two Dimensional Conjugated Polymeric Nanocrystals for Organic Electronics

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SI 1. Materials

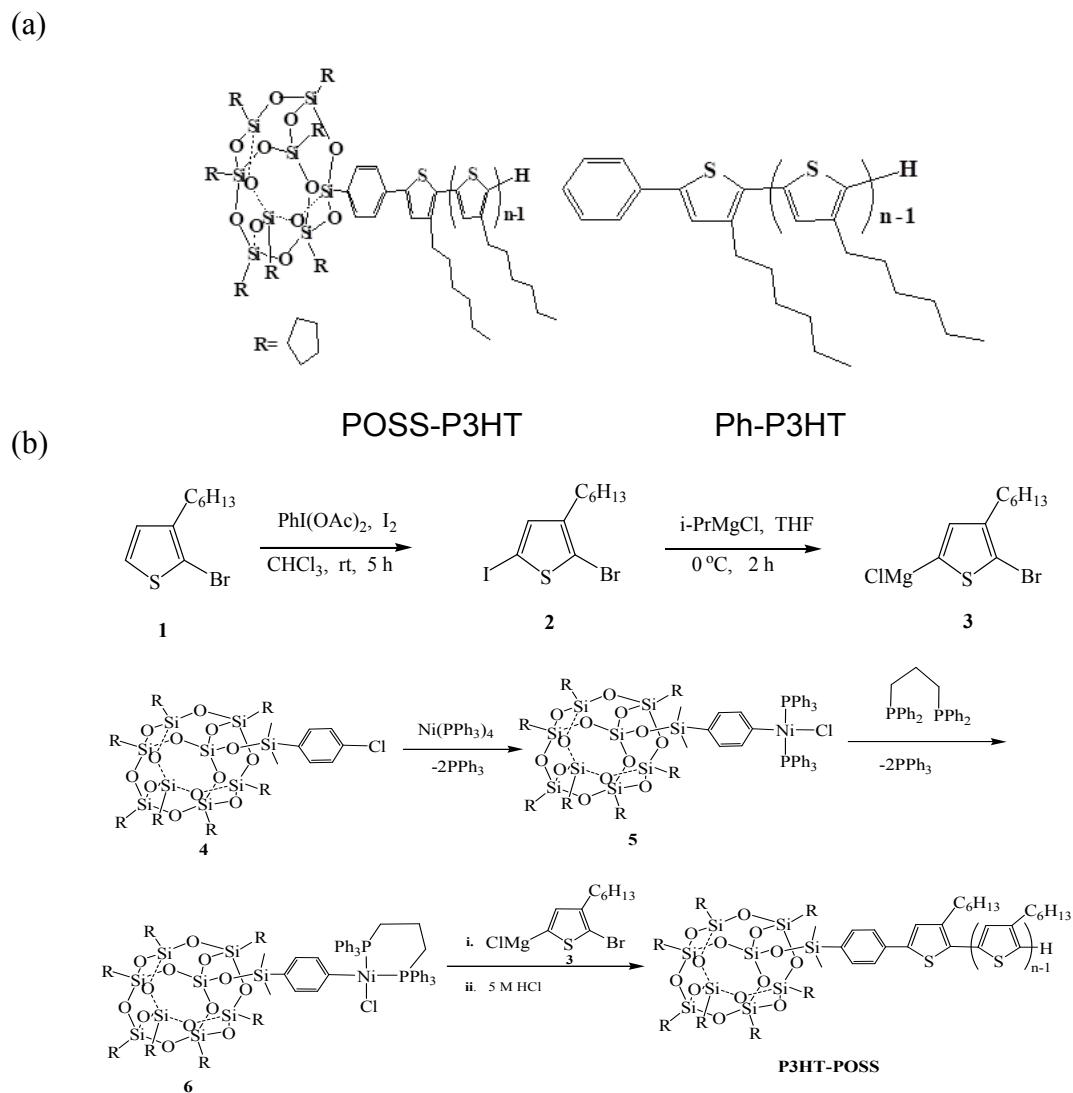
P3HT ($M_n=22000$ g/mol, PDI=2.3) and PC₆₁BM were purchased from 1-Material Inc. PEDOT:PSS was purchased from Heraeus. All materials are used as received without further purification.

SI 2. Synthesis and characterization of POSS-P3HT and Ph-P3HT

Materials: 2-bromo-3-hexylthiophene (97%), isopropylmagnesium chloride solution (2.0 M in tetrahydrofuran (THF)), iodobenzene 1,1-diacetate (98%), sodium thiosulfate (99%), tetrakis(triphenylphosphine)nickel(0), 1,3-bis(diphenylphosphino)propane (97%) and 1-(chlorophenyl)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (97%) were from Aldrich and used as received without further purification. Toluene (EMD, ACS grade) and THF (EMD, ACS grade) were purified by distillation from CaH₂ and Na, respectively. All other chemicals were analytical grade reagents.

Materials characterization: ¹H NMR and ¹³C NMR spectra were recorded using a Varian Mercury 300 MHz spectrometer and CDCl₃ as the solvent and referenced to the solvent residual peak (CDCl₃: ¹H: δ = 7.27 ppm, ¹³C: δ = 77.23 ppm). Gel permeation chromatography (GPC) was performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/103/104 Å), mixed bed (103/104/106 Å)] and a double detector system with THF as eluent at a flow rate of 1.0 mL/min at 30 °C. The detector system consisted of a differential refractometer (Waters 410) and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories).

Synthesis of POSS-P3HT: The synthetic routes of monomers and polymers are presented in **Scheme 1**. The initiators and regioregular P3HT are synthesized according to the procedure described in literature.^[S1-S3]



Scheme S1. (a) Molecular structures of POSS-P3HT and Ph-P3HT, and (b) the synthetic routes of POSS-P3HT

2-Bromo-3-hexyl-5-iodothiophene (2). 2-Bromo-3-hexylthiophene (2.3 g, 9.341 mmol) was dissolved in 50 mL of chloroform, and then mixed with iodine (1.304 g, 5.138 mmol) and

iodobenzene diacetate (1.805 g, 5.604 mmol). The solution was stirred at room temperature for 5 hours (hrs), and then poured over aqueous sodium thiosulfate. The aqueous layer was washed twice with ether, and the organic layers were collected, dried, filtered and roto-evaporated. The residual solution was filtered through silica using hexanes as eluent. After evaporation and drying under vacuum, 3.37 g (97%) of product was obtained. **Figure S1** shows the ^1H NMR spectrum of 2-bromo-3-hexyl-5-iodothiophene. ^1H NMR (CDCl_3 , δ): 6.96 (s, 1H), 2.52 (t, 2H), 1.54 (m, 2H), 1.30 (m, 6H), 0.89 (t, 3H).

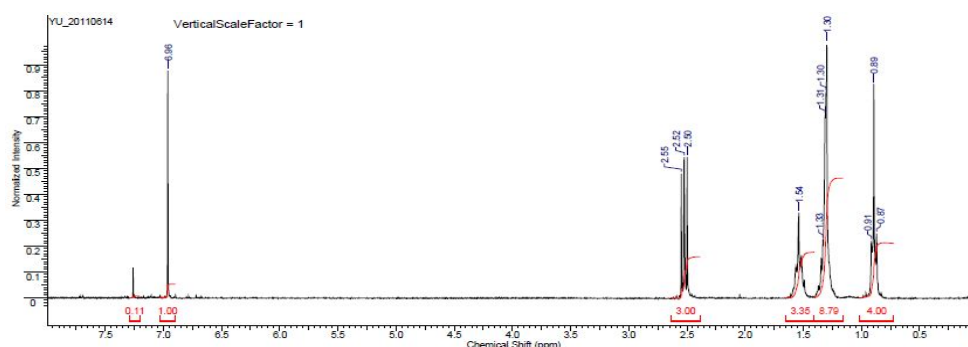


Fig. S1. The ^1H NMR spectrum of 2-bromo-3-hexyl-5-iodothiophene

Regioregular head-to-tail poly(3-hexylthiophene) with POSS as an end group (P3HT-POSS).

Under an argon atmosphere, tetrakis(triphenylphosphine)nickel(0) (16.00 mg, 0.014 mmol) and 1-(Chlorophenyl)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (67.30 mg, 0.067 mmol) were dissolved in 2 mL of dry toluene. The color of the reaction solution changed from deep red to light yellow gradually and the solution was stirred for 20 hrs. 1,3-bis(diphenylphosphino)propane (10 mg, 0.024 mmol) was added to above solution and stirred for 3 hrs.

Under an argon atmosphere, 2-bromo-3-hexyl-5-iodothiophene (373 mg, 1 mmol) was dissolved in dry THF (10 mL) and cooled down to 0 °C under stirring. Isopropylmagnesiumchloride (0.5 mL, 1 mmol) was added dropwise over 5 min and stirring continued for 2 hrs. Then the crude initiator **6** solution was added rapidly via syringe. The reaction was allowed to warm to room temperature and stirred overnight. 1 mL of 5 M HCl was added to quench the polymerization. The mixture solution was stirred for 30 minutes (min) and poured into 100 mL of cold methanol. The precipitates were filtered, washed with methanol and cold hexane, respectively. The products were dissolved in toluene and passed through a column packed with alumina, Celite and silica gel. The column was eluted with toluene. The combined polymer solution was concentrated to 20 mL and was poured into cold methanol (200 mL). The precipitates were collected by filtration and dried *in vacuo* to afford a purple solid (85 mg). The polydispersity index of POSS-P3HT is shown in **Figure S2**.

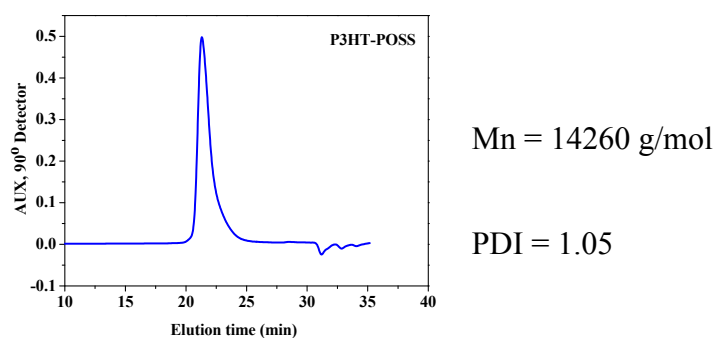


Fig. S2. The polydispersity index of POSS-P3HT.

^1H NMR (300 MHz, CDCl_3 , δ): 7.59 (d, $J = 8.1$, ArH), 7.35 (d, $J = 8.5$, ArH), 6.97 (s, 1H, ArH), 2.80 (t, $J = 4.2$, 2H, CH_2), 1.84-1.35 (m, CH_2), 0.91 (s, 3H, CH_3). ^{13}C NMR (300 MHz, CDCl_3 , δ): 139.88, 133.70, 130.49, 128.59, 77.23, 76.97, 76.72, 67.94, 31.67, 30.48, 29.44, 29.23, 25.59, 22.62, 14.07.

Regioregular head-to-tail poly(3-hexylthiophene) with phenyl and hydrogen as an end groups (Ph-P3HT).

The preparation of P3HT-Ph was similar to that for P3HT-POSS. The polydispersity index of Ph-P3HT is shown in **Figure S3**.

^1H NMR (300 MHz, CDCl_3 , δ): 7.60 (d, $J = 7.2$, ArH), 7.38 (t, $J = 7.7$, ArH), 7.16 (s, ArH), 6.98 (s, 1H, ArH), 6.90 (s, ArH), 6.83 (m, ArH), 2.81 (m, 2H, CH_2), 2.62 (t, $J = 7.7$, CH_2), 2.54 (m, CH_2), 1.71 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.35 (m, 4H, CH_2), 0.92 (m, 3H, CH_3).

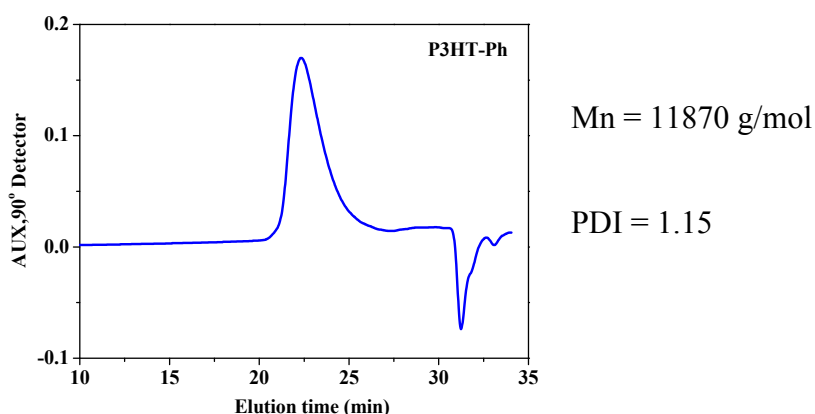


Fig. S3. The polydispersity index of Ph-P3HT

X-ray diffraction (XRD) was also applied to investigate the structure of the Ph-P3HT. **Fig. S4** shows the XRD patterns of Ph-P3HT. The Ph-P3HT shows a (100) reflection peak owing to the lamellar layered structure. ^[s4] Similarly, the (200) and (300) diffraction peaks indicate the crystallinity of Ph-P3HT with edge-on chain orientation. ^[S5] The out-of-plane reflection

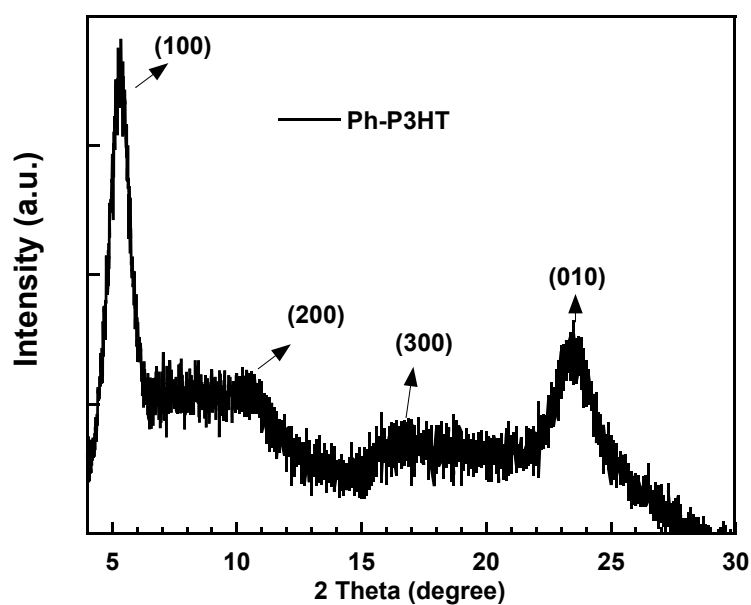


Fig. S4. X-ray diffraction spectra of Ph-P3HT.

peak of (010) is due to $\pi - \pi$ interchain stacking. ^[s6]

Characterization of POSS-P3HT thin film

UV-vis absorption spectra of POSS-P3HT and Ph-P3HT thin films were recorded using HP 8453 UV-vis spectrophotometer. **Figure S5** presents UV-vis absorption spectra of POSS-P3HT and Ph-P3HT thin films. It is clear that POSS-P3HT and Ph-P3HT have a identical absorption spectrum, indicating POSS has no influence on band structure of P3HT.

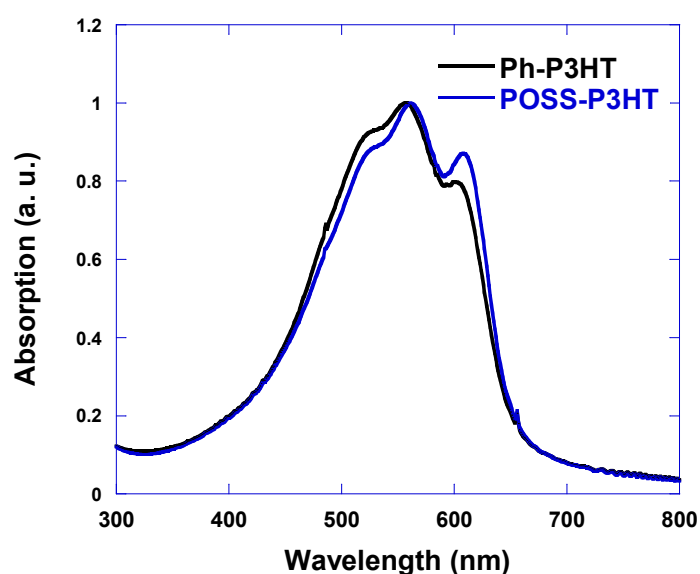


Fig. S5. The absorption spectra of POSS-P3HT and Ph-P3HT thin films

The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of POSS-P3HT thin film are estimated by cyclic voltammetry (CV) measurements. The electrochemical cyclic voltammetry (CV) of POSS-P3HT thin film was measured with three electrodes system (Pt disk as working electrode, Pt wire as counter electrode, and Ag/AgCl reference electrode). The electrolyte is a 0.1 mol·L⁻¹ tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) in MeCN, and the

ferrocene/ferrocenium (Fc/Fc^+) was used for calibration, under an argon atmosphere with a scan rate of 100 mV/s.

Figure S6 presents the current-voltage curve of POSS-P3HT thin film. Based on oxidation and reduction potentials, The HOMO energy level of -4.87 eV and the LUMO energy level of -3.0 eV are estimated for POSS-P3HT. Both HOMO and LUMO levels of POSS-P3HT are consistent with those reported from P3HT,^[s7] indicating that the band gap of POSS-P3HT was not altered by incorporating POSS.

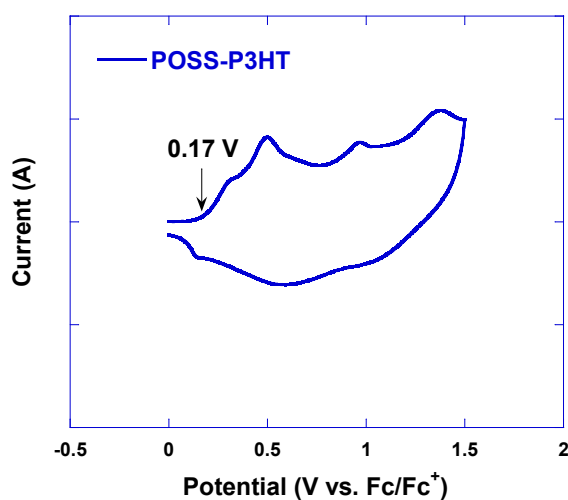


Fig. S6. The cyclic voltammetry curves of POSS-P3HT thin film

To investigate the thermal properties of POSS-P3HT, the thermogravimetric analysis (TGA) measurements were performed under N₂ atmosphere. **Figure S7** reveals that all three P3HT losses weight at ~450°C, and at 600 °C, a 35.9% residue for Ph-P3HT, a 29.1% residue for POSS-P3HT, a 22.8% residue for P3HT. The TGA results suggest that POSS-P3HT possesses relatively better thermal stability compared to P3HT, although slightly lower than Ph-P3HT.

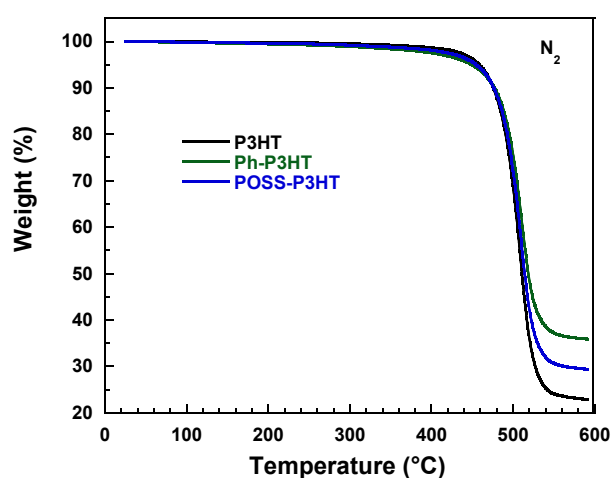


Fig. S7. TGA graph of P3HT, Ph-P3HT and POSS-P3HT.

To further investigate the thermal properties of POSS-P3HT, the differential scanning calorimetry (DSC) were also performed. The heating and cooling DSC curves for all three polymers are shown in **Figure S8**. As has been reported,^[s8] P3HT exhibits one melting peak at 180 °C in heating cycle and forms one glass state upon cooling cycle. The as-synthesized Ph-P3HT and POSS-P3HT also exhibit one melting peak when undergoing heating process, but with higher values of melting point than P3HT.

The results from both TAG and DSC measurements suggest that Ph-P3HT and POSS-P3HT possess better thermal properties than P3HT.

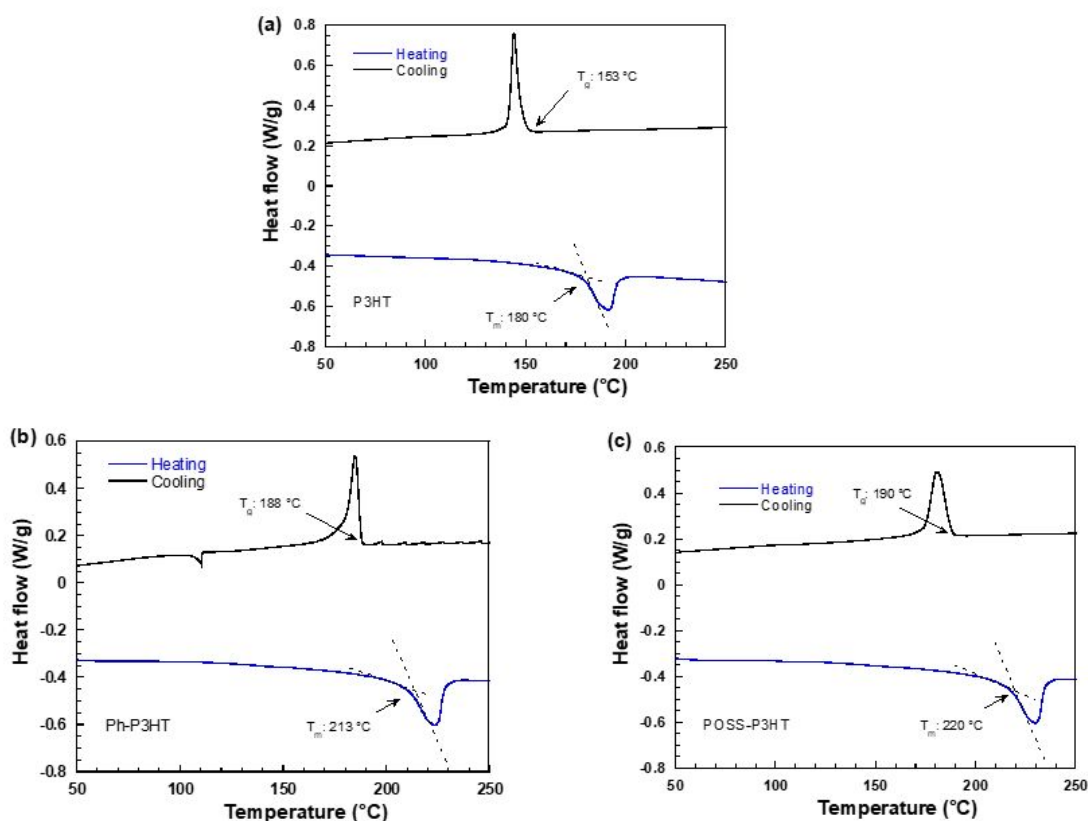


Fig. S8. DSC heating and cooling traces of (a) P3HT, (b) Ph-P3HT and (c) POSS-P3HT at a scanning speed of 10 °C/min under N₂.

SI 3. Preparation and Characterization of Thin Films

The POSS-P3HT and POSS-P3HT:PC₆₁BM, P3HT:PC₆₁BM and Ph-P3HT:PC₆₁BM composite thin films were spin cast from o-dichlorobenzene (CB) solutions. The 1D WAXD pattern of POSS-P3HT crystals were captured were obtained by using a Bruker AXS Dimension D8 X-Ray System. Transmission electron microscopy images of POSS-P3HT crystals were captured by a JEOL transmission electron microscopy using an accelerating voltage of 120 kV. Scanning electron microscopy images were captured by FEI-Philips scanning transmission electron microscope, Model Tecnai T12T/STEM. Atomic force microscopy images were taken on a Nanoscope NS3A system (Digital Instrument).

SI 4. Fabrication and characterization of two-terminal diodes

The hole-only device with a device structure of ITO/PEDOT:PSS/polymer/MoO₃/Ag, where MoO₃ is molybdenum trioxide and Ag is silver. Over 30 nm thick MoO₃ ensures sufficient segregation between perovskite and Ag electrode, is fabricated and characterized. The current versus voltage (*I-V*) characteristics of above devices are measured in dark by a Keithley model 2400 source measure unit.

Figure 5a presents the *I-V* curves of the hole-only devices fabricated by pristine polymer thin films. As shown in **Figure 5a**, an ohmic-contact region under low external biases is represented by the linear *I-V* characteristics, followed by a TFL region with increased injection current, in which all the traps have been filled up. The carrier mobilities of polymer thin films are estimated with equation of $J = \frac{9}{8}\epsilon_r\epsilon_0\mu_0\frac{V^2}{L^3}$, where *J* is the dark current density, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, μ_0 is the zero-field mobility, and *L* is the thickness of the active layer, respectively. The hole mobilities of $\sim 4 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$, $\sim 2 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ and $\sim 1 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ are observed from POSS-P3HT 2D nanosheets, and P3HT and Ph-P3HT thin films, respectively.

The film morphology of P3HT, Ph-P3HT and POSS-P3HT were studied by atomic force microscopy (AFM). The AFM height images are shown in **Fig. S9**. It is found that the root

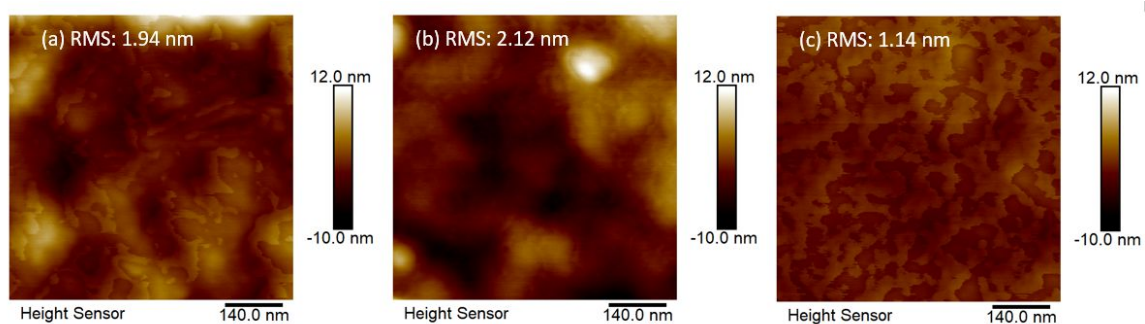


Fig. S9. AFM height images of (a) P3HT, (b) Ph-P3HT and (c) POSS-P3HT thin films.

mean square (RMS) values of P3HT, Ph-P3HT and POSS-P3HT are 2.12, 1.94 and 1.14 nm, respectively. A smaller RMS value implies that the POSS-P3HT possesses a smoother surface.

SI 5. Fabrication and characterization of thin film transistors

The concentrations of polymers in dichlorobenzene solutions are 1.0 mg/mL. The “bottom-contact” thin film transistors device structure was treated in hexamethyldisilazane before deposition of polymers thin films. The FET structures with different source-drain separations were fabricated on an n-doped Si wafer; the n-doped Si was used as the gate. The gate dielectric was a 200 nm film of SiO₂ thermally grown directly on the wafer. Source and drain electrodes (Au) were deposited on the SiO₂ by e-beam evaporation. The channel lengths (source-drain separation) ranged between 5 and 25 μm, and the channel width was 1000 μm. Electrical measurements were carried out using a Keithley 4200 Semiconductor Characterization System in ambient air.

The field-effect mobility in the saturation regime was extracted using the equation $I_{DS} = C_i \mu (V_{GS} - V_{Th})^2 W/2L$, under the condition of $-V_{DS} > -(V_{GS} - V_{Th})$, where I_{DS} is the source/drain current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of gate dielectric layer, and V_{GS} , V_{Th} and V_{DS} are the gate, threshold, and source/drain voltages, respectively. **Figure 5b** presents I_{DS} vs. V_G characteristics of TFTs made by POSS-P3HT 2D nanosheets, and P3HT and Ph-P3HT thin films. The field-effect

hole mobilities of $\sim 8.5 \times 10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$, $\sim 1.2 \times 10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$ and $\sim 3.4 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ are observed from POSS-P3HT 2D nanosheets, and P3HT and Ph-P3HT thin films, respectively.

SI 6. Fabrication and Characterizations of Organic Photovoltaics

Organic photovoltaics with a device structure of ITO/PEDOT:PSS/BHJ composite/Al were fabricated and characterized. The ITO substrates were cleaned in an ultra-sonic bath with acetone, detergent, de-ionized water and isopropanol, subsequently. After dried in oven overnight, the pre-cleaned ITO substrates were treated in an UV-ozone incubator. Then, PEDOT:PSS thin films with a thickness around 40 nm were deposited atop the ITO substrates, followed by thermal annealing at 150 °C for 15 minutes. The BHJ composites of POSS-P3HT:PC₆₁BM, P3HT:PC₆₁BM and Ph-P3HT:PC₆₁BM thin films were deposited atop the PEDOT:PSS thin films from corresponding solutions. Finally, ~ 100 nm Al was thermally deposited through a shadow mask in a vacuum chamber with a base pressure of 2.0×10^{-6} mbar. The device area was measured to be 4.5 mm². The current density versus voltage (J-V) characteristics of OSCs were measured by a Keithley 2400 source meter under AM 1.5 G spectrum from a class solar simulator (Japan, SAN-EI, XES-40S1) with the light intensity of 100 mW/cm². The light intensity was calibrated by a Newport certified reference silicon cell (PV Measurements, with KG-5 visible filter). The statistical data from over 30 identical solar cells based on P3HT:PC₆₁BM, Ph-P3HT PC₆₁BM and POSS-P3HT PC₆₁BM in **Fig. S10**.

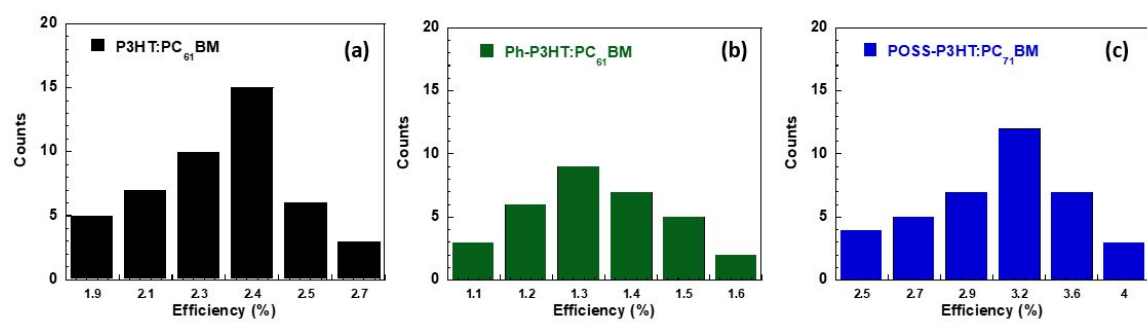


Fig. S10. Statistical distribution of solar cells based on (a) P3HT:PC₆₁BM, (b) Ph-P3HT:PC₆₁BM, (c) POSS-P3HT:PC₆₁BM

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