

Supporting Information for

**Self-Assembly and Ring-Opening Metathesis Polymerization of
Cyclic Conjugated Molecules on Highly Ordered Pyrolytic Graphite**

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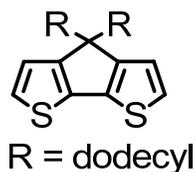
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General methods

p-Xylene and 2nd generation Grubbs catalyst were purchased from Sigma-Aldrich. TiCl₄ was purchased from Aencore Chemical. Phenylloctane was purchased from TCL. These chemicals were used without further purification. Synthesis was performed under nitrogen atmosphere using standard Schlenk techniques. Synthesis and characterization of the cyclic conjugated molecules and conjugated polymers with *n*-hexyl or 2-ethylhexyl chains were performed on the basis of the method described in the literature.^{S1} The cyclic monomers with *n*-dodecyl or *n*-octadecyl chains were prepared by McMurry reaction using TiCl₄/Zn in THF under a nitrogen atmosphere and purified by preparative size exclusion chromatography (SEC) using JAI LC-9204 with a column GAIGEL-1H-40 eluted with chloroform (flow rate = 14 mL min⁻¹). ¹H NMR spectra were obtained using a Bruker 500 MHz spectrometer. MALDI-TOF mass spectra were recorded by Bruker Daltonics, Autoflex III smartbeam LRF200-CID. ESI mass spectra were recorded by Fourier transform ion cyclotron resonance (FT-ICR Mass; VARIAN 901-MS). Polymer molecular weight was determined by gel permeation chromatography (GPC) using a JASCO 880-PU and a JASCO 870-UV detector (referenced to polystyrene standards with THF eluent).

Reference S1: S. W. Chang and M. Horie, *Chem Commun*, 2015, **51**, 9113-9116.

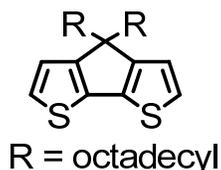
Synthesis of 4,4-didodecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene



4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (CPDT) (100 mg, 0.56 mmol) was dissolved in 2.8 mL of anhydrous THF. *n*-Butyllithium 2.5 M in hexane (0.23 mL, 1.02 equiv.) was added dropwise at 0 °C. The solution was stirred at 0 °C for 30 min and at room temperature (r.t.) for 30 min. It was then cooled to 0 °C and 1-dodecylbromide (140 mg, 0.14 mL, 1.0 equiv.) was added dropwise. The reaction mixture was stirred at r.t. for 3.5 hr. The second alkylation was followed by same procedure. After THF was removed, the product was extracted with hexane and DI water. The crude product was purified by column chromatography on silica gel using hexan as the eluent. After dried

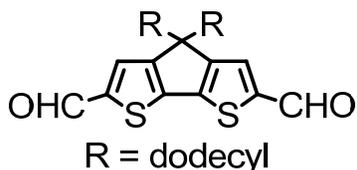
in vacuum, the compound was obtained as orange liquid (364 mg, 63%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.12 (d, $J = 4.5$ Hz, 2H, 2-CPDT), 6.9 (d, $J = 5$ Hz, 2H, 3-CPDT), 1.79 (m, 4H, CH_2), 0.9-1.25 (m, 40H, CH_2), 0.86 (t, $J = 7$ Hz, 6H, CH_3).

Synthesis of 4,4-dioctadecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene



4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (CPDT) (100 mg, 0.56 mmol) was dissolved in 2.8 mL of anhydrous THF. *n*-Butyllithium 2.5 M in hexane (0.23 mL, 1.02 equiv.) was added dropwise at 0 °C. The solution was stirred at 0 °C for 30 min and at r.t. for 30 min. It was then cooled to 0 °C and 1-octadecylbromide (187 mg, 0.2 mL, 1.0 equiv.) was added dropwise. The reaction mixture was stirred at r.t. for 3.5 hr. The second alkylation was followed by same procedure. After THF was removed, the product was extracted with hexane and DI water. The crude product was purified by column chromatography on silica gel using hexane as the eluent. After dried in vacuum, the compound was obtained as green solid (344 mg, 90%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.12 (d, $J = 4.5$ Hz, 2H, 2-CPDT), 6.9 (d, $J = 5$ Hz, 2H, 3-CPDT), 1.79 (m, 4H, CH_2), 0.9-1.3 (m, 64H, CH_2), 0.86 (t, $J = 7$ Hz, 3H, CH_3).

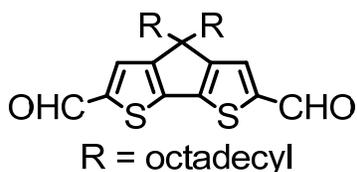
Synthesis of 4,4-didodecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene -2,6-dicarbaldehyde



4,4-Didocyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (258 mg, 0.5 mmol, 1.0 equiv.) was dissolved in anhydrous ether (5 mL, 0.1 M) with tetramethylethylenediamine (0.16 mL, 2.1 equiv.). *n*-Butyllithium 2.5 M in hexane (0.42 mL, 2.1 equiv.) was added dropwise at 0 °C. The solution was stirred at 0 °C for 30 min and then at r.t. for 30 min. It was then cooled to 0 °C and DMF (0.14 mL, 3.5 equiv.) was added dropwise. The reaction mixture was stirred at r.t. overnight under nitrogen atmosphere. After solvent was removed, the product was extracted with ether and DI

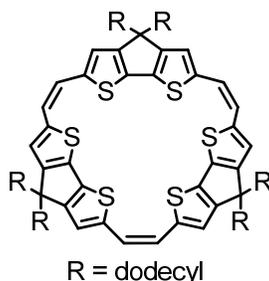
water. The crude product was purified by column chromatography on silica gel using hexane and ethylacetate (2:1) as the eluent. After dried in vacuum, the compound was obtained as caramel solid (239 mg, 84%). ¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 2H, -C=O), 7.6 (s, 2H, 3-CPDT), 1.79 (m, 4H, CH₂), 0.9-1.3 (m, 40H, CH₂), 0.86 (t, *J* = 7 Hz, 6H, CH₃).

Synthesis of 4,4-dioctadecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene -2,6-dicarbaldehyde



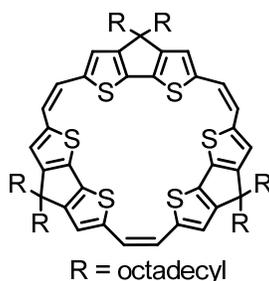
4,4-Dioctadecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (300 mg, 0.44 mmol, 1.0 equiv.) was dissolved in anhydrous ether (4.4 mL, 0.1 M) with tetramethylethylenediamine (0.14 mL, 2.1 equiv.). *n*-Butyllithium 2.5 M in hexane (0.37 mL, 2.1 equiv.) was added dropwise at 0 °C. The solution was stirred at 0 °C for 30 min and then at r.t. for 30 min. It was then cooled to 0 °C and DMF (0.12 mL, 3.5 equiv.) was added dropwise. The reaction mixture was stirred at r.t. overnight under nitrogen atmosphere. After solvent was removed, the product was extracted with ether and DI water. The crude product was purified by column chromatography on silica gel using hexan and Ethyl acetate (2:1) as the eluent. After dried in vacuum, the compound was obtained as orange solid (265 mg, 81%). ¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 2H, -C=O), 7.6 (s, 2H, 3-CPDT), 1.88 (m, 4H, CH₂), 0.9-1.3 (m, 64H, CH₂), 0.86 (t, *J* = 7 Hz, 6H, CH₃).

Synthesis of CPDTV-C12



TiCl₄ (0.07 mL, 10 equiv.) was added to a suspension of zinc (0.1 g, 22.5 equiv.) in THF (6.7 mL, 0.01 M) at 0 °C under nitrogen with stirring over a period of 30 min. The suspension was heated to reflux for 1 h. To the gently refluxing suspension, a solution of 4,4-didodecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6- dicarbaldehyde (38.0 mg, 0.067 mmol, 1.0 equiv.) and pyridine (0.15 mL) in THF (3 mL) was added. After reflux for 1 hour, the reaction mixture was cooled to r.t. The reaction mixture was concentrated to remove THF in vacuum. The residue was then purified by the flash silica gel column with acetone as eluent. The residue was further purified by chromatography on a silica gel column using hexane as eluent and SEC to give CPDTV-C12 as purple oil (6 mg, 11 %). ¹H NMR (500 MHz, CDCl₃): δ 6.72 (s, 6H, vinyl), 6.68 (s, 6H, 3-CPDT), 1.75 (m, 12H, CH₂), 0.9-1.30 (m, 120H, CH₂), 0.85 (t, *J* = 7 Hz, 18H, CH₃). MS (FD) spectrum: [C₁₀₅H₁₆₂S₆+H]⁺ (*m/z*): found: 1616.

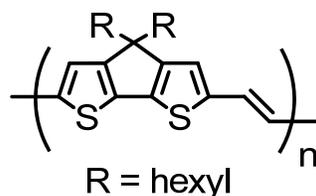
Synthesis of CPDTV-C18



CPDTV-C18 was synthesized by the similar method to CPDTV-C12 using TiCl₄ (0.15 mL, 10 equiv.) and zinc (0.2 g, 22.5 equiv.) in THF (4.5 mL, 0.03 M), 4,4-dioctadecyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6- dicarbaldehyde (100 mg, 0.135 mmol, 1.0 equiv.) and pyridine (0.3 mL) in THF (2 mL). ¹H NMR (500 MHz, CDCl₃): δ 6.72 (s, 6H, vinyl), 6.68 (s, 6H, 3-CPDT), 1.75 (m, 12H, CH₂), 0.9-1.30 (m,

192H, CH₂), 0.85 (t, $J = 7$ Hz, 18H, CH₃). HRMS (FD) spectrum: [C₁₄₁H₂₃₄S₆+H⁺] (m/z): 2120.6713, found: 2120.6734 (error 1.0 ppm).

Synthesis of poly(CPDTV-C6)



Second-generation Grubbs catalyst (13.6 mg, 1.0 equiv.) was dissolved in anhydrous *p*-xylene (0.67 mL, 0.024 M) in a 10 mL Schlenk tube under nitrogen. This solution was added to CPDTV-C6 (18 mg, 0.016 mmol, 1.0 equiv.) in a 5 mL Schlenk tube. After stirred at 120 °C for 6 min, ethylvinyl ether (3.0 mL) was added to quench the reaction and stirred at r.t. for 10 min. The reaction mixture was then washed with methanol and acetone, then precipitated into methanol to provide the blue powder (10 mg, 56 %). ¹H NMR (500 MHz, CDCl₃): δ 6.98 (s, 2H, vinyl), 6.84 (s, 2H, 3-CPDTV), 1.8-0.96 (m, 20H, CH₂), 0.80 (br, 6H, CH₃). GPC (polystyrene standards in THF): $M_n = 3000$, $M_w/M_n = 1.3$.

STM sample preparation and observation

STM was performed using a JEOL JSPM-5200, with a handmade liquid cell for the solid-liquid interface measurements. STM tips were made by mechanically cutting Pt/Ir (80/20) wire (0.3mm in diameter) from Nilaco Corporation. All STM images were processed with line averaging and brightness adjustment by WinSPM software.

The cyclic conjugated molecules (CPDTV-C6, CPDTV-C12, CPDTV-C18, or CPDTV-EH) were dissolved in 1-phenyloctane with the concentration of 1×10^{-4} M. The solution (8 droplets, c.a. 0.15 mL) was deposited onto the freshly cleaved high oriented pyrolytic graphite (HOPG) surfaces fixed in the handmade cell. The substrate was annealed at 90 °C for 5 min and cooled down to room temperature, then was put on the machine stage. The STM tip was immersed in the solution to record images at the solid-liquid interface without any solvent evaporation (Figs. 2 and S1).

For the observation of ROMP using a polymer solution without purification, the sample was prepared as follows. The second generation Grubbs catalyst (1.5 mg, 1.0 equiv.) was dissolved in anhydrous *p*-xylene (36 μL, 0.05 M) in a Schlenk tube under

nitrogen. This solution was added to CPDTV-C6 (2 mg, 1.0 equiv.) in another Schlenk tube. After the reaction mixture was stirred at 120 °C for 6 min, the reaction mixture was immediately cooled to stop the polymerization and 18 μL of the solution was diluted in phenyloctane on the HOPG with concentration about 1×10^{-4} M (c.a. 1 mg based on the monomer/9 mL phenyloctane). STM images were recorded at the solid-liquid interface without any solvent evaporation (Figs. 3a and S3a). ^1H NMR (500 MHz, CDCl_3): δ 7.52-7.2 (m, Grubbs cat.), δ 7.04-6.98 (m, 2H, vinyl *cis*- and *trans*-), 6.89-6.84 (m, 2H, 3-CPDT, *cis*- and *trans*-), 1.8-0.92 (m, 20H, CH_2), 0.8 (br, 6H, CH_3). GPC (polystyrene standards in THF): $M_n = 2200$, $M_w/M_n = 1.26$.

ROMP of CPDTV-C12 was also performed by similar methods using the second generation Grubbs catalyst (0.89 mg, 1.0 equiv.), *p*-xylene (25 μL , 0.05 M), and CPDTV-C12 (1.7 mg, 1.0 equiv.) heated at 120 °C for 3 min. 1×10^{-4} M (c.a. 0.5 mg based on the monomer/6 mL phenyloctane) was casted on HOPG and STM images were recorded (Fig. S3b).

ROMP of CPDTV-C18 was also performed by similar methods using the second generation Grubbs catalyst (0.8 mg, 1.0 equiv.), *p*-xylene (20 μL , 0.05 M), and CPDTV-C18 (16 mg, 1.0 equiv.) heated at 120 °C for 6 min. 1×10^{-4} M (c.a. 1 mg based on the monomer/5 mL phenyloctane) was casted on HOPG and STM images were recorded (Fig. S3c).

ROMP was performed for the self-assembled monolayer of CPDTV-C6 on HOPG. The sample was prepared as follows. CPDTV-C6 was dissolved in hexane with the concentration of 1×10^{-4} M (0.4 mg/3.6 mL), then the solution was casted on the freshly cleaved HOPG surface. After drying solvent, the second generation Grubbs catalyst/*p*-xylene solution (49 mM, 0.3 mg/7.2 μL) was casted on to the HOPG surface and heated at 120 °C for 1 min to perform ROMP on the substrate. After *p*-xylene was dried, phenyloctane (8 drops, c.a. 0.15 mL) was poured to the substrate. STM images were recorded at the solid-liquid interface without any solvent evaporation (Figs. 3b and S3d).

DFT calculation

DFT calculations for monomers and polymers were conducted using Gaussian 09W package software [Functional/basis set: B3LYP/6-31G(d)] and a supercomputer

in Research Center for Computational Science, Okazaki, Japan. For the calculations of electronic states and geometrical optimization of molecules shown in Figs. 4 and S9, the dihexyl side chains of all the molecules were replaced to dimethyl ones to reduce computational costs without influencing the energy of HOMO and LUMO, both of which are located only at the conjugated rings or conjugated main chains. For the optimization of CPDTV-C6, CPDTV-C12, CPDTV-C18, and CPDTV-EH monomers, the optimized geometry of the dimethyl terminated cyclic monomer was reused by replacing the dimethyl side chains to C6, C12, C18, and EH ones. Packing models shown in Fig. 2 and Fig. S2 were constructed based on the STM images (Fig. S1) and the optimized structures of each molecules; the molecules are placed on bright spots seen in STM images with no overlap and interaction of each side chains. Note that obtaining more sophisticated packing structure requires a calculation with HOPG substrate surface, adsorption geometry and a unit cell of the molecules, and boundary condition, etc, which, however, should be based on STM images with much better high resolution. We are going to obtain such STM images and will report in the next publication.

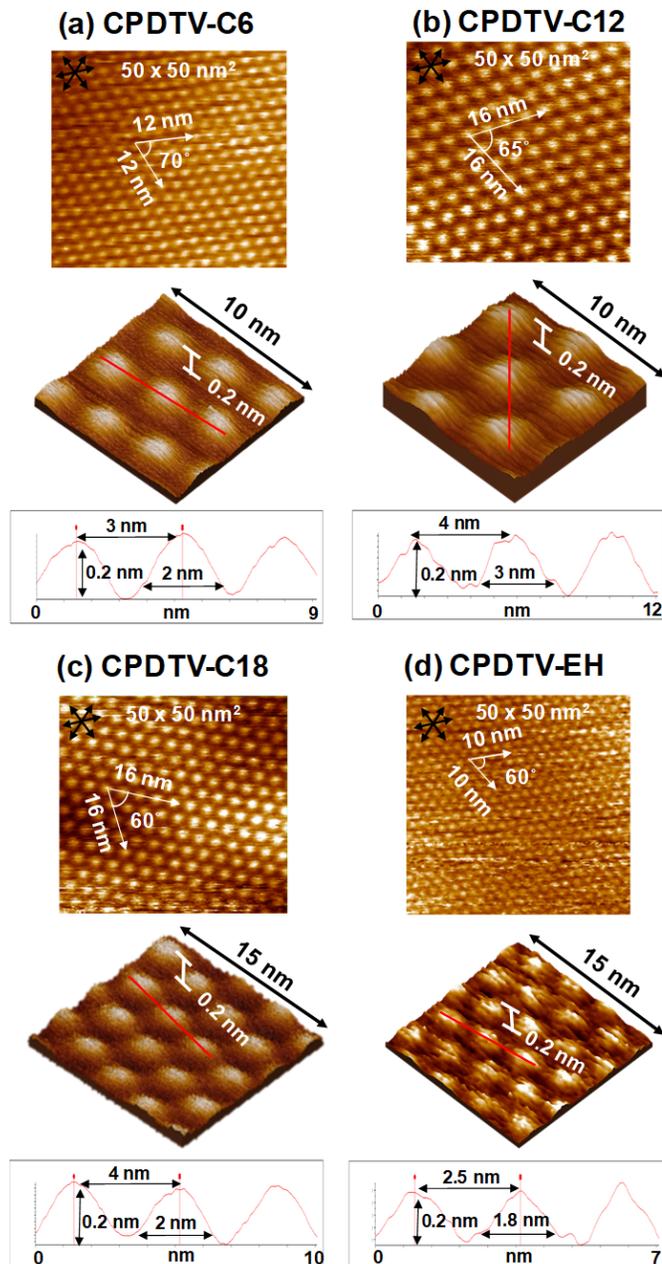


Fig. S1 STM topographic images and cross-section profiles of (a) CPDTV-C6, (b) CPDTV-C12, (c) CPDTV-C18, and (d) CPDTV-EH at the 1-phenyloctane/HOPG interface. The lattice direction of the graphite is indicated at top left of the STM images. White arrows represent the distance corresponding to 5 molecules. Conditions: $I_{\text{set}} = 0.5$ nA, $V_{\text{bias}} = -0.5$ V for CPDTV-C6; $I_{\text{set}} = 0.51$ nA, $V_{\text{bias}} = -0.39$ V for CPDTV-C12; $I_{\text{set}} = 0.065$ nA, $V_{\text{bias}} = 0.904$ V for CPDTV-C18; $I_{\text{set}} = 0.3$ nA, $V_{\text{bias}} = -0.8$ V for CPDTV-EH. Molecular structures and packing models of (a) CPDTV-C6, (b) CPDTV-C12, (c) CPDTV-C18, and (d) CPDTV-EH obtained from molecular modeling calculations.

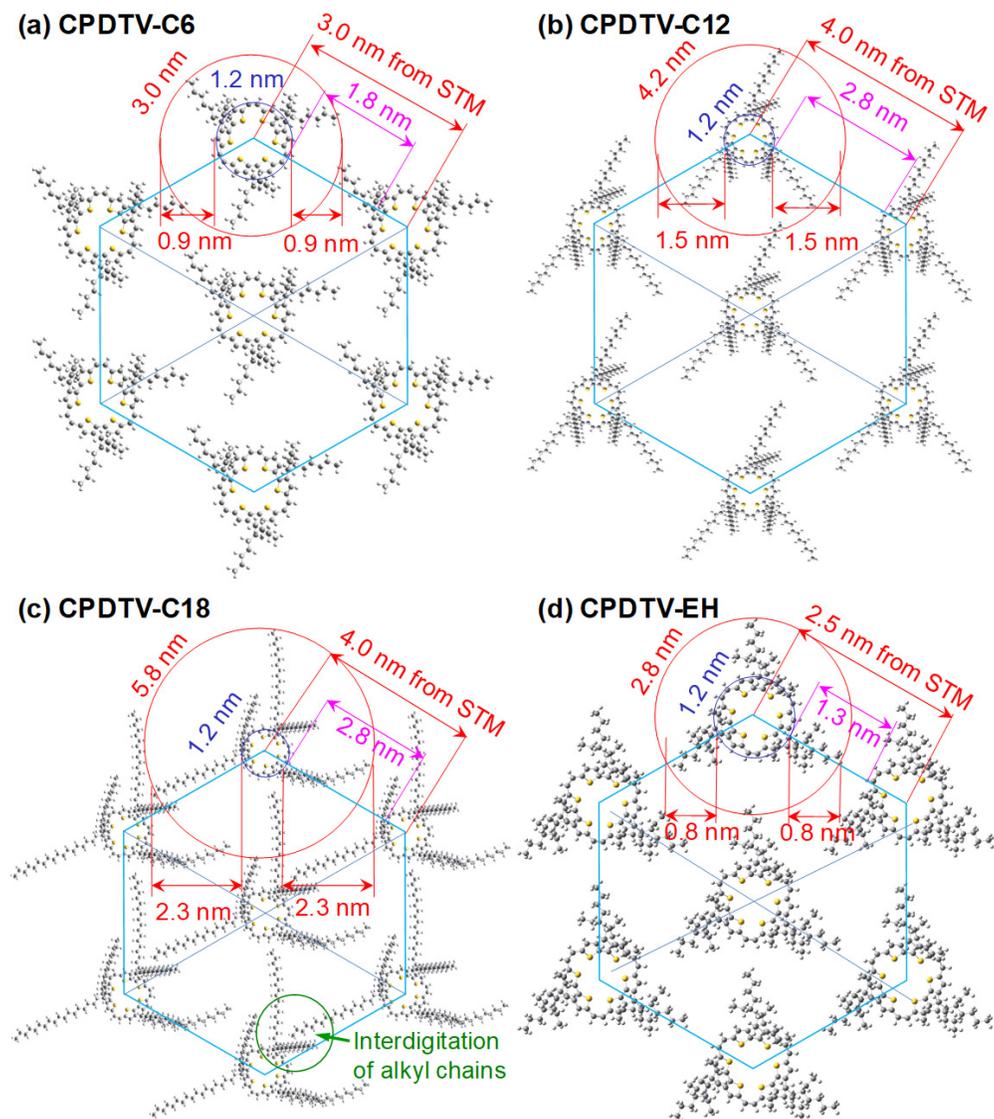
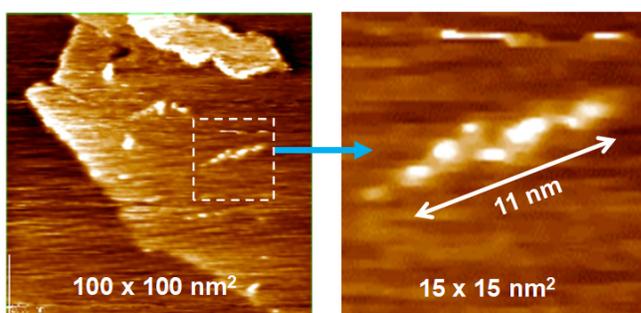
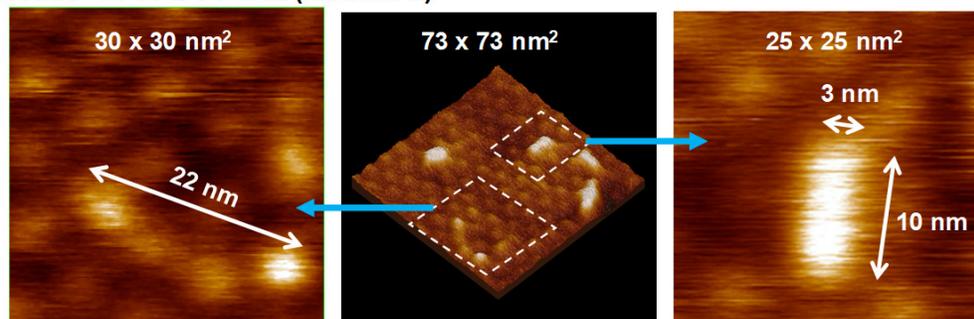


Fig. S2 Molecular structures of (a) CPDTV-C6, (b) CPDTV-C12, (c) CPDTV-C18 and (d) CPDTV-EH and their packing models obtained from STM images (Fig. S1).

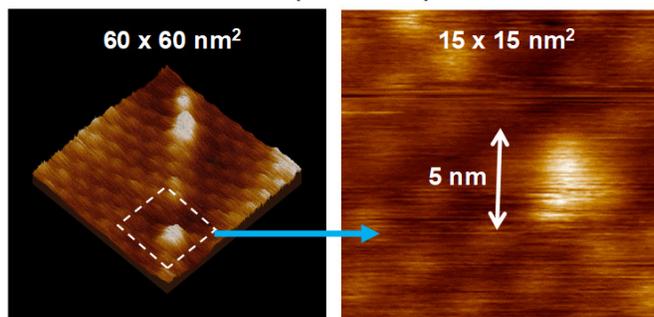
(a) ROMP of CPDTV-C6 (Method 2)



(b) ROMP of CPDTV-C12 (Method 2)



(c) ROMP of CPDTV-C18 (Method 2)



(d) ROMP of CPDTV-C6 on HOPG (Method 3)

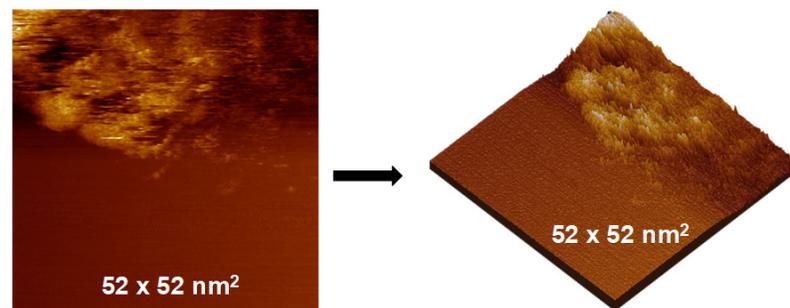


Fig. S3 STM images after ROMP of (a) CPDTV-C6 ($I_{\text{set}} = 0.33 \text{ nA}$, $V_{\text{bias}} = 0.47 \text{ V}$), (b) CPDTV-C12 ($I_{\text{set}} = 0.07 \text{ nA}$, $V_{\text{bias}} = 0.84 \text{ V}$), (c) CPDTV-C18 ($I_{\text{set}} = 0.10 \text{ nA}$, $V_{\text{bias}} = 0.50 \text{ V}$), and (d) CPDTV-C6 on HOPG ($I_{\text{set}} = 0.20 \text{ nA}$, $V_{\text{bias}} = 0.50 \text{ V}$). (e) Approximate size of the possible chemical structures.

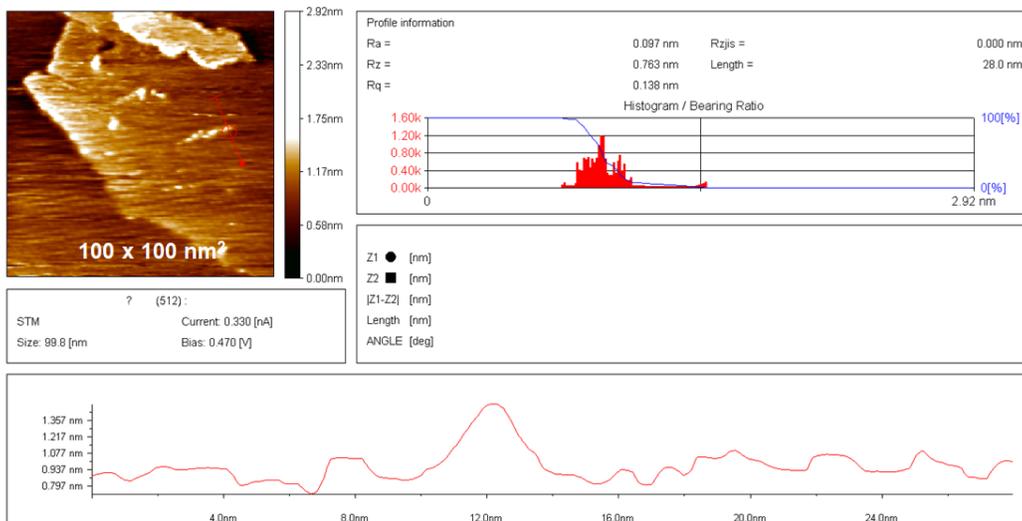


Fig. S4 STM image and cross-section profile after ROMP of CPDTV-C6 ($I_{\text{set}} = 0.33$ nA, $V_{\text{bias}} = 0.47$ V).

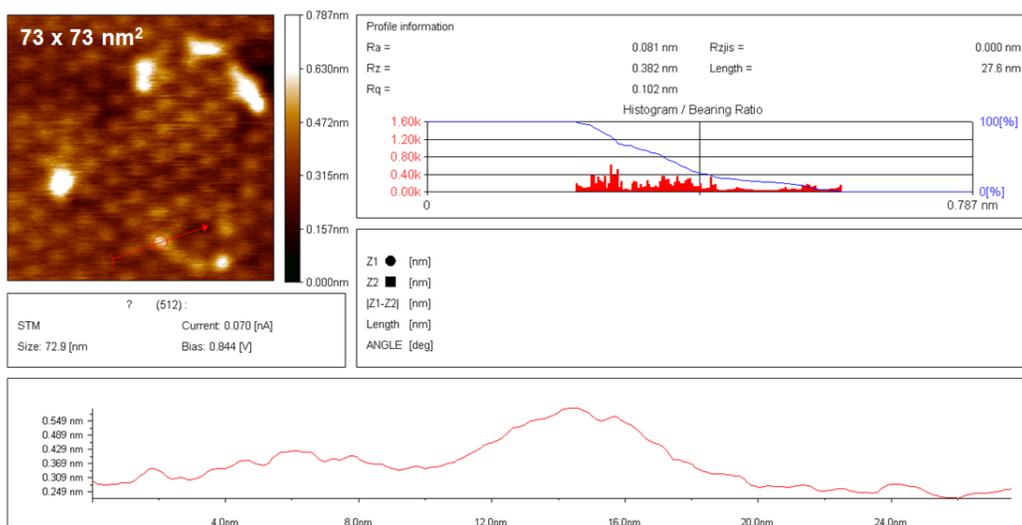


Fig. S5 STM image and cross-section profile after ROMP of CPDTV-C12 ($I_{\text{set}} = 0.07$ nA, $V_{\text{bias}} = 0.84$ V).

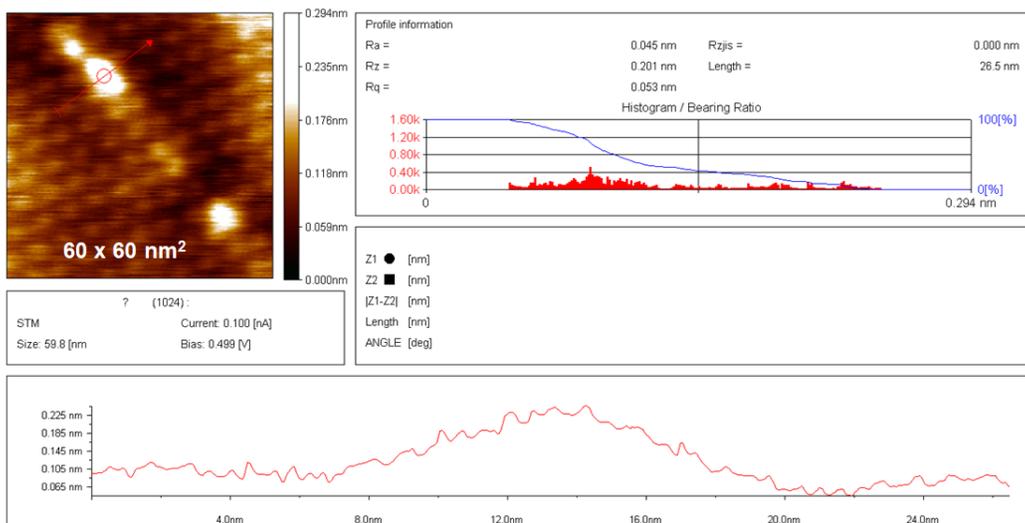


Fig. S6 STM image and cross-section profile after ROMP of CPDTV-C18 ($I_{set} = 0.10$ nA, $V_{bias} = 0.50$ V).

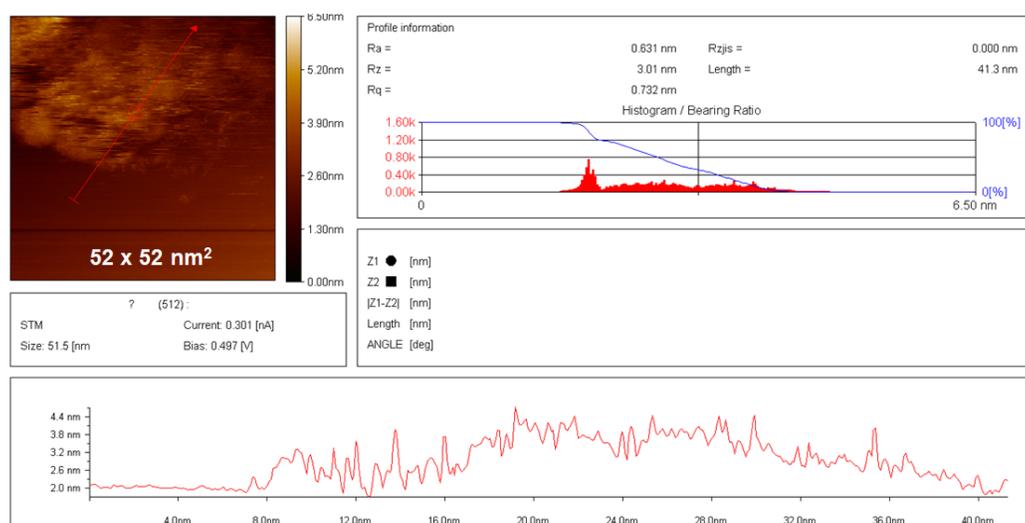


Fig. S7 STM image and cross-section profile after ROMP of CPDTV-C6 on HOPG ($I_{set} = 0.20$ nA, $V_{bias} = 0.50$ V).

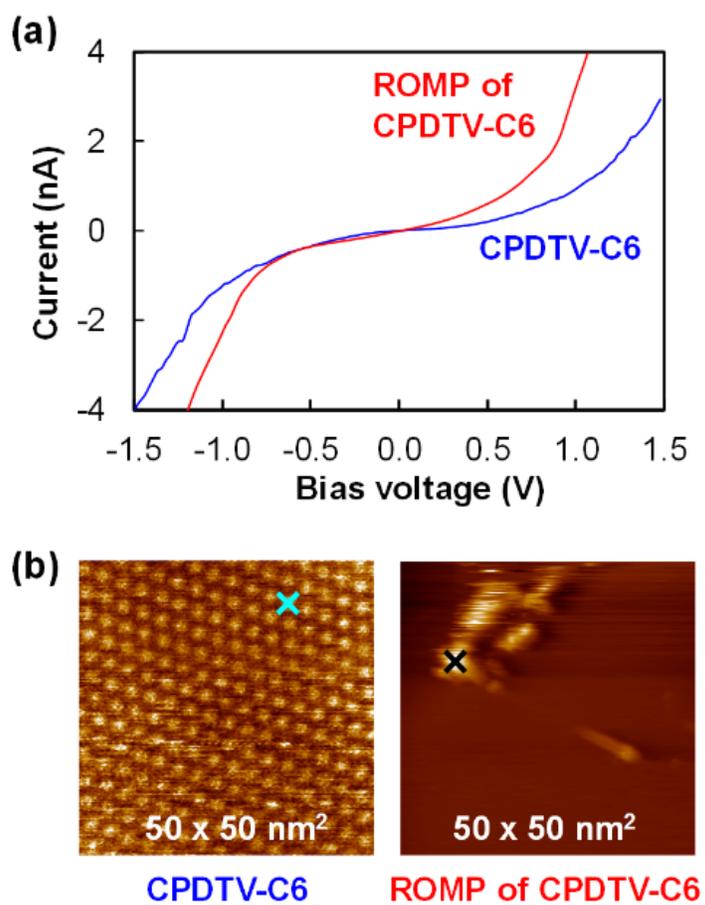


Fig. S8 Scanning tunneling spectra. (a) I - V curves of CPDTV-C6 and its ROMP product recorded during STM measurements. (b) STM images for the STS measurement (topographic image set point: $I_{\text{set}} = 0.5$ nA, $V_{\text{bias}} = 0.604$ V for the monomer. $I_{\text{set}} = 0.3$ nA, $V_{\text{bias}} = -0.5$ V for the polymer).

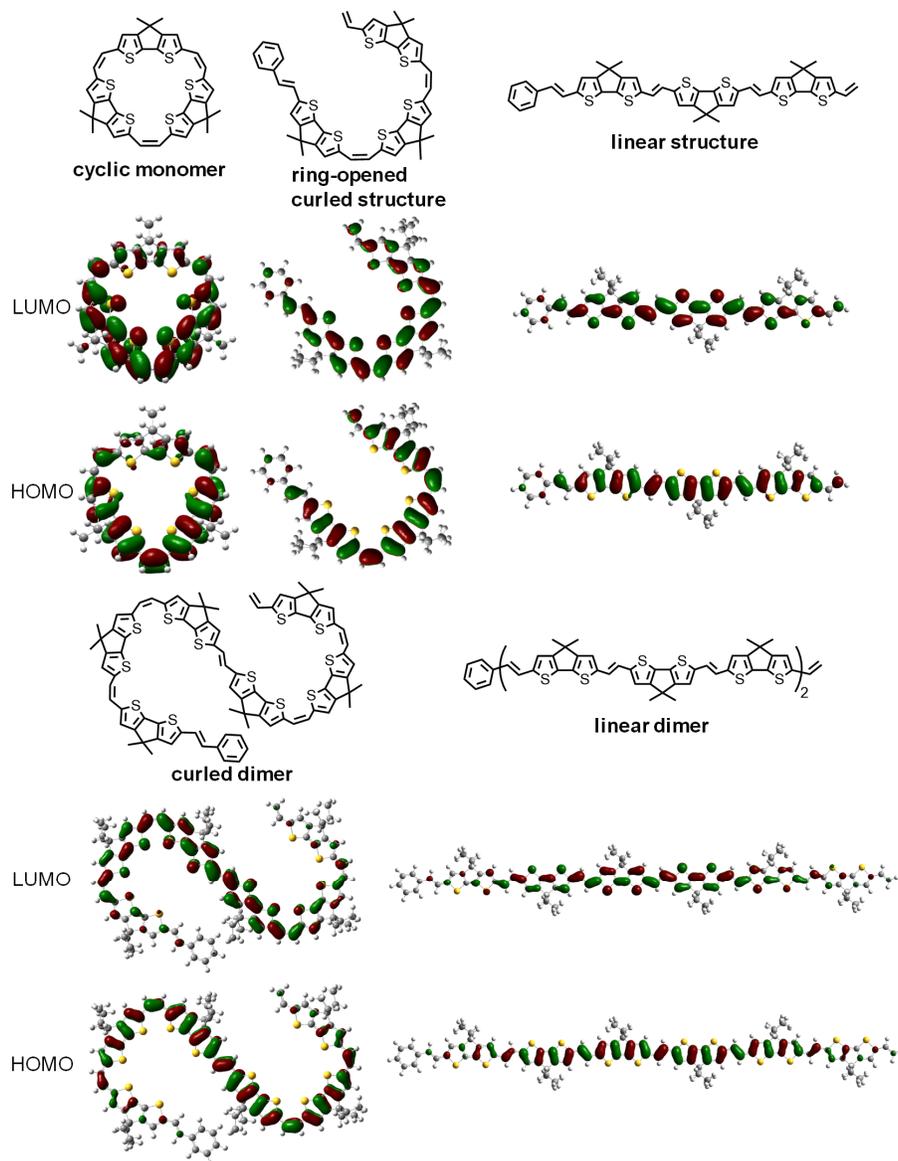


Fig. S9 Molecular orbital distributions of HOMO and LUMO for the cyclic monomer and predicted ROMP products.

AFM sample preparation and observation

AFM was performed using a Park XE-70 AFM. AFM probes (PPP-RT-NCHR, silicon material, tip radius < 7 nm) were purchased from AMPLE GOAL INTERNATIONAL CO., LTD. All AFM images were processed with line averaging and brightness adjustment by XEI software.

For the observation of ROMP, the samples were prepared as follows. CPDTV-C6 was dissolved in hexane with the concentration of 1×10^{-4} M (0.8 mg/7 mL), then the solution was casted on the freshly cleaved HOPG surfaces. After drying the solvent, the second generation Grubbs catalyst/*p*-xylene solution [40 mM (0.1 mg/30 μ L), 24 mM (0.6 mg/30 μ L), 33 mM (0.4 mg/ 14 μ L), or 49 mM (1mg/24 μ L)] was casted on to the HOPG surface and heated at 120 °C for 1 min until the solvent evaporated (Fig. 5).

Furthermore, three different sample preparation methods were applied using non-purified polymer, purified polymer without monomer layer, and purified polymer with monomer layer (Fig. S10).

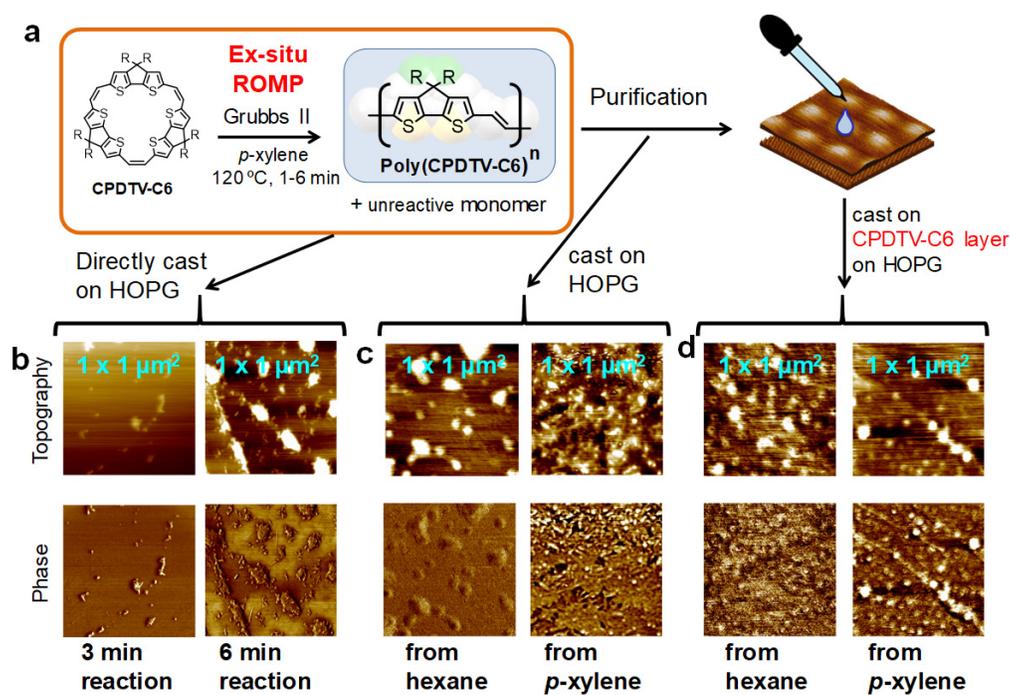


Fig. S10 (a) Schematic illustration of sample preparation. (b) AFM images of the reaction mixture after 3 min and 6 min reaction. The reaction mixture was diluted with hexane and casted on HOPG. Unreacted monomer molecules were first adsorbed on HOPG, followed by adsorption of resulting polymers on the monomer layer. (c) AFM images of purified polymer without monomer layer. Purified polymer was deposited from hexane or *p*-xylene solution on HOPG. (d) AFM images of purified polymer with monomer layer. After deposition of the monomer layer, purified polymer was deposited from hexane or *p*-xylene solution on HOPG.

For the observation of ROMP using a non-purified polymer, the samples were prepared as follows. The second generation Grubbs catalyst (3mg, 0.25 equiv.) was dissolved in anhydrous *p*-xylene (0.28 mL, 0.05 M) in a Schlenk tube under nitrogen. This solution was added to CPDTV-C6 (16 mg, 1.0 equiv.) in another Schlenk tube. After stirring at 120 °C for 3 min or 6 min, the reaction mixture was immediately cooled to stop the polymerization. The mixture (1.0 mg) was diluted in 5 mL hexane on the HOPG with concentration about 1×10^{-4} M and AFM observation was conducted (Fig. S5b).

For the observation using the purified polymer, poly(CPDTV-C6) was dissolved in hexane or *p*-xylene with concentration c.a. 1×10^{-4} M. This solution was casted on the freshly cleaved HOPG (Fig. S10c) or the CPDTV-C6 treated HOPG (Fig. S10d).

In comparison between Fig. 5 and Fig. S10, AFM images of the surface polymerization films were significantly different from the drop-casted films of the purified polymer on HOPG.

First, the reaction mixture of ROMP was directly drop casted on the surface without purification. Here, the same condition was applied in the STM observation of the ROMP polymers (Fig. 2). As shown in Fig. S10b, the AFM image from 3 min ROMP reaction exhibited stretched polymer chains with 20-150 nm length. These stretched polymer chains might be on the unreacted monomer layer on HOPG. Large sphere shaped clusters (150-200 nm) with many shorter polymer chains (50-70 nm length) were observed in the AFM image from 6 min ROMP. These results indicate processes of propagation and aggregation. At the initial stage of ROMP, the polymer chains were propagated maintaining their stretched shape, and they stuck on the monolayer on HOPG. After longer reaction time, the polymer chains form sphere clusters losing π - π interaction between the polymers and a monomer layer on HOPG.

Second, to verify the interaction between the polymer and the monomer monolayer on HOPG, the polymer was purified from the reaction mixture of ROMP to remove the unreacted monomer. After deposition of the monomer layer from hexane solution and the purified polymer from hexane or *p*-xylene solution, AFM was conducted. As shown in Fig. S10c, the purified polymer randomly aggregated when the polymer was deposited from hexane solution onto the bare HOPG without preparation of the monomer layer. This is probably due to lack of inducement of the monomer layer to the polymer. The ROMP polymer was less soluble in hexane compared to *p*-xylene. Therefore, the large aggregations of the polymer were observed using the hexane solution. On the other hand, the purified polymer was deposited from *p*-xylene solution without preparation of the monomer layer on HOPG. The polymer fibres were formed on the bare HOPG (Fig. S10c), probably due to crystalline property of the polymer. In this case, interactions between the polymer chain and HOPG may be minor.

Third, the purified polymer was casted on the monomer layer on HOPG. Sphere polymer clusters with 70-100 nm size were observed with slight regularity on the

monomer layer on HOPG (Fig. S10d). This may be accounted for by the inducement of the monomer layer to the polymer clusters as well as excluded-volume interaction between the polymer clusters, though linear stretched polymer chains were not observed. These experiments further proved the monomer layer indeed have the effect to induce the regular deposition of the polymer.