- SUPPORTING INFORMATION -

Macrocyclic Regioregular Poly(3-hexylthiophene): From Controlled Synthesis to Nanotubular Assemblies.

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This Supporting Information (SI) describes:

1. Materials
2. Characterization techniques
3. Experimental aspects of the synthesis
4. SI Figures

1. Materials

2-Bromo-3-hexylthiophene (Acros, 98%), N-iodosuccinimide (Acros, 98%), isopropylmagnesium chloride solution (Acros, solution 2.0M in THF), *N,N*-dimethylformamide (Sigma-Aldrich, > 99%), phosphorus oxychloride (purum, >98%, Fluka), sodium acetate (anhydrous, Sigma-Aldrich, >99%), tetrakis(triphenylphosphine) nickel(0) ($Ni(PPh_3)_4$, Aldrich), propane-1,3-diylbis(diphenylphosphane) (dppp, Acros), *p*-toluene sulfonic acid monohydrated (Acros), *p*-bromoacetophenone (VWR, 98%), ethylene glycol (Acros, 98%) were used as received. THF and toluene solvents were dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

2. Characterization techniques

^{1}H-spectra were recorded using both a Bruker AMX-300 and 500 apparatus at r.t. in $CDCl_3$

(30mg/0.6ml). Size exclusion chromatography (SEC) was performed in THF at 35°C using a Triple Detection Polymer Laboratories liquid chromatograph equipped with a refractive index (ERMA 7517), a capillary viscometry, a light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC-RI/CV / RALS) and an automatic injector (Polymer Laboratories GPC-RI/UV) and four columns : a PL gel 10 μm guard column and three PL gel Mixed-B 10 μm columns (linear columns for separation of MW_{PS} ranging from 500 to 10^6 daltons). UV-Visible absorption spectra were taken onto a Cary-WinUV50 spectrophotometer from 500 to 300 nm. Both linear and cyclic P3HT were characterized by solution preparation in chloroform (1 mg/ml, 23°C). Gas chromatography analysis was performed with a GCQ type from Finnigan (Interscience) equipped with Rtx-5Sil MS column (30 m, 0.25 mm, 0.25 μm) in 5/95 polydiphenylsiloxane/polydimethylsiloxane. The heating program started at 60°C for 1 min, followed by a ramp of 10°C/min until 250°C and an isotherm at 250°C for 2 min. Injector temperature was fixed at 250°C. Helium was used as mobile phase with a 30cm/s rate. 2 μl of the sample were introduced in the column and the experiment was operating in positive mode EI+ (electronic ionization) and CI+ (chemical ionization) with an electronic energy of 70eV. In CI+ mode, methane was used as the reactive gas and the temperature of the source was hold at 200°C. The transfer line was maintained at 260°C. MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 mW delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10.000. All the samples were analyzed using trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malonitrile (DCTB), that matrix was prepared as 20 mg/ml solution in CH_2Cl_2. The matrix solution (1 μl) was applied to a stainless steel target and air dried. Polymer samples were dissolved in CH_2Cl_2 to obtain 1 mg/ml solutions. 1μl aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 100 to 3000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained. Atomic Force Microscopy: Sub-monolayer deposits were prepared by solution casting (10 μl to 20 μl) from dilute chloroform solutions (from 0.02 to 0.2 $g.L^{-1}$) on freshly-cleaved muscovite mica or highly-oriented pyrolytic graphite, at room temperature in a solvent-saturated atmosphere. AFM studies were carried out in Tapping-Mode with Multimode Nanoscope IIIa or ICON microscopes (Bruker) operating in air at room temperature, using microfabricated silicon cantilevers with a spring constant of around 30 $N.m^{-1}$ (RTESP or NCHV, Veeco). Images of different areas of the samples were collected and Nanoscope image processing software was used for image analysis. Tentative molecular models shown in Fig. 6 of the manuscript were built using the Materials Studio 5.0

package from Accelrys. Chain and macrocycle were built by means of molecular mechanics geometry optimizations, using the Forcite module with the COMPASS force field and convergence criterion on energy of 10^{-3} kcal/mol. [COMPASS : Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies, based on a) Sun, H. *J. Phys. Chem. B.* **1998**, *102*, 7338. b) Bunte, S.W.; Sun, H. *J. Phys. Chem. B.* **2000**, *104*, 2477]. Differential scanning calorimetry (DSC) measurements were acquired on a DSC Q200 apparatus from TA Instruments under nitrogen flow at heating rate 10°C/min from -30 to 250°C.

3. Experimental aspects of the synthesis

- Monomer, initiator and catalyst synthesis

Preparation of *p*-bromoactophenone ethylene ketal: The GRIM initiator was prepared similarly to the procedure described by Detty *et al*. (cfr. Reference part : ref.10)

^{1}H-NMR (300 Hz, $CDCl_3$): 7.50-7.25 (m, 4H), 4.1-3.5 (m, 4H), 1.62 (s, 3H)

Preparation of 2-bromo-3-hexyl-5-iodothiophene: N-iodosuccinimide (5.45g, 24.24 mmol) was added to a stirred solution of 2-bromo-3-hexylthiophene (5.00 g, 20.2 mmol) in a mixture 7:3 of CHCl3 and acetic acid (50 mL) at 0°C, and the mixture was stirred in the dark at room temperature for 4h. Then 10% aqueous $Na_2S_2O_3$ was added, and the mixture was extracted with Et_2O. The organic layer was washed with 10% aqueous $Na_2S_2O_3$ and dried over anhydrous $MgSO_4$. After filtration, the solvent and iodobezene were removed by evaporation under reduced pressure. The residue was purified by silica gel column chromatography (eluent: heptane) to give 2-bromo-3-hexyl-5-iodothiophene as pale yellow oil (6.90 g, 92%).

^{1}H-NMR (300 Hz, $CDCl_3$): 6.97 (s, 1H), 2.54 (t, ^3J =7.5 Hz, 2H), 1.56 (quint, 2H), 1.32 (m, 6H), 0.89 (t, ^3J =6.4 Hz, 3H).

Preparation of *trans*-bromo(*p*-acetophenone ethylene ketal)-1,3-bis(diphenylphosphino)propane nickel (II): The experimental procedure has been chosen identical to the one described in Ref 9 (See reference in main paper) by using toluene as solvent.

- Synthesis of linear and cyclic poly(3-hexylthiophene)s 1, 2 and 3

Synthesis of α-ketal poly(3-hexylthiophene) : Into a flask under nitrogen atmosphere containing 2-bromo-3-hexyl-5-iodothiophene (1,18 g, 3,15 mmol) was added dry THF (15.0 mL) via a syringe, and the mixture was stirred at 0°C. i-PrMgCl (2.0 M solution in THF, 1,08 mL, 3,15 mmol) was added via a syringe, and the mixture was stirred at 0°C for 0.5h. A suspension of Ni complex (4.6 mol%) in THF (5.0 mL) was added to the mixture via a syringe at 0°C, and then the mixture was stirred at room temperature. After the reaction mixture was stirred for 1 day, a 5N HCl aqueous solution was quickly added to quench the reaction. The mixture was stirred for 0.5h more then precipitated in cold MeOH. The product was washed well with MeOH to afford a purple solid, > 98.5% rr-HT-P3HT.

- Yield = 69%

- UV ($CHCl_3$, nm): 446

- MALDI-ToF Analysis : cfr. Main text and Figure 1a

- SEC analysis (apparent molecular weight value) : Mn = 5,1 kg/mol; PDI = 1.10

Synthesis of α-keto poly(3-hexylthiophene) 1 : Into a flask 400 mg of α-ketal poly(3-hexylthiophene) (1.05×10^{-4} mol) are dissolved by 80 ml of THF and 3 ml of water. After solubilization, *p*-TosOH (15 mg, 0.5×10^{-4} mol) is then added and the solution is kept under stirring. After 48 hours, the medium is concentrated and the polymer is precipitated out from cold MeOH.

- Yield = 99%

- UV ($CHCl_3$, nm): 446

- MALDI-ToF Analysis : cfr. Main text and Figure 1b

- SEC analysis (apparent molecular weight value): Mn = 5,0 kg/mol; PDI = 1.12

Formyl-de-hydrogenation of α-keto poly(3-hexylthiophene) 1 : α-Keto poly(3-hexylthiophene) **1** (Mn_{MALDI}=3,6 kg/mol, PDI=1.12) (300 mg, 0.071 mmol) was dissolved in anhydrous toluene (80 mL) under N_2. *N,N*-Dimethylformamide (1 mL, 13 mmol) and $POCl_3$ (0.7 mL, 7.6 mmol) were added. The reaction was carried out first at 75°C for 50h. The solution was cooled down to room temperature, followed by the adding of saturated aqueous sodium acetate solution. The solution was stirred for another 2h. The polymer **2** was precipitated in cold methanol and washed well with water, then methanol.

- Yield = 94%

- SEC analysis (apparent molecular weight value) : Mn = 6,0 kg/mol; PDI = 1.14

- ^{1}H-NMR (500 Hz, $CDCl_3$): cfr. Main text and Figure 2

Cyclization of P3HT 2: A solution containing P3HT **1** (150 mg, 3.75×10^{-5} mol) in 50 ml of THF is slowly added to a funnel containing 100 ml of THF. The content of the secondary funnel is simultaneously added to a refluxing solution (Temp. ~ 75°C) containing 500 ml of THF, 10 mg of NaOH (3.8×10^{-4} mol), 500 mg of water and 5 ml of pure ethanol. The addition of the P3HT **2** into the basic solution is totally performed after 12h. The medium is then allowed for stirring during an extra 12 hours. After completion, the medium is cooled down to room temperature and concentrated prior the final precipitation on cold methanol of the as-obtained cyclic P3HT **3**.

- Yield = 96%

- SEC analysis (apparent molecular weight value): Mn = 5,7 kg/mol; PDI = 1.11

- ^{1}H-NMR (500 Hz, $CDCl_3$): cfr. Main text and Figure 3

4. SI Figures

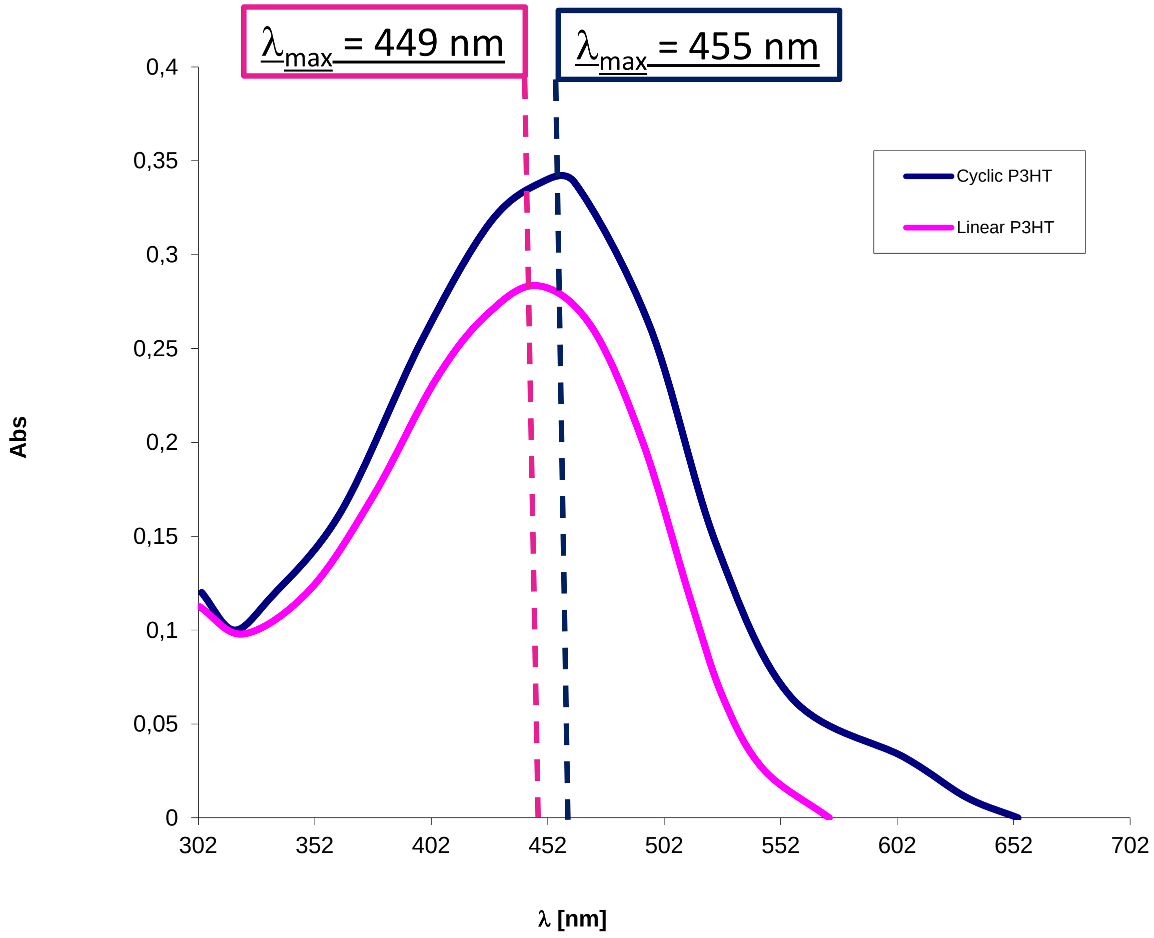

Figure S1 : UV/Vis spectra ($CHCl_3$, T = 298K) of P3HT **2** (linear P3HT) and corresponding P3HT **3** (cyclic P3HT) (M_n = 3.6 kg/mol).

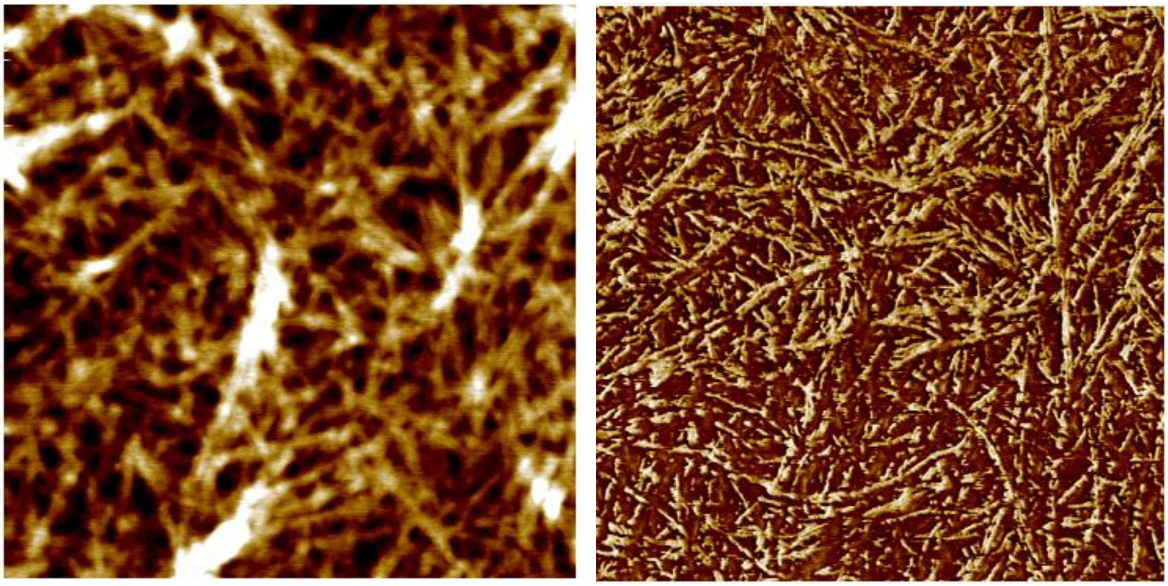

Figure S2 : 2.0x2.0 μm² TM-AFM image of a deposit of **2** on mica, showing the fibrillar morphology at larger scale than in the MS. Left: height image (vertical scale bar : 20 nm); right : phase image (vertical scale bar 60°).

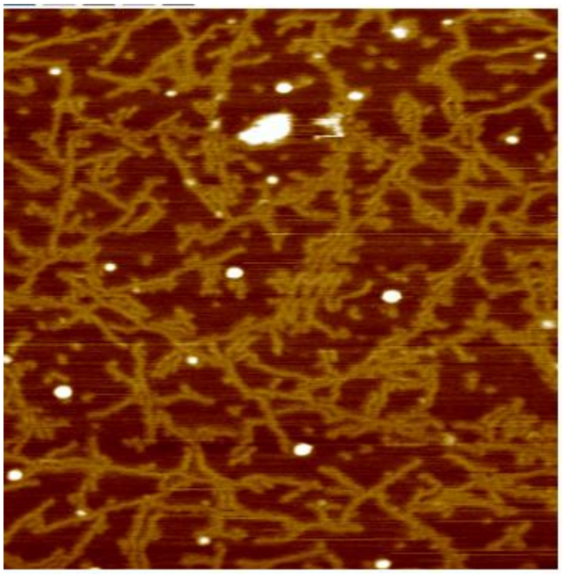

Figure S3 : 1.2x 1.2 μm² TM-AFM height image (vertical scale bar : 5 nm) of a deposit of **3** on mica, showing longer tubes than shown in Figure 3 of the MS. The mica substrate appears dark brown.