Electronic Supplementary Material (ESI) for RSC Advances.

Engineering Porous and Compact Two-Dimensional Nanoarchitectures on Surfaces Taking Advantage of BisTerpyridine-Derivatives Self-Assembly

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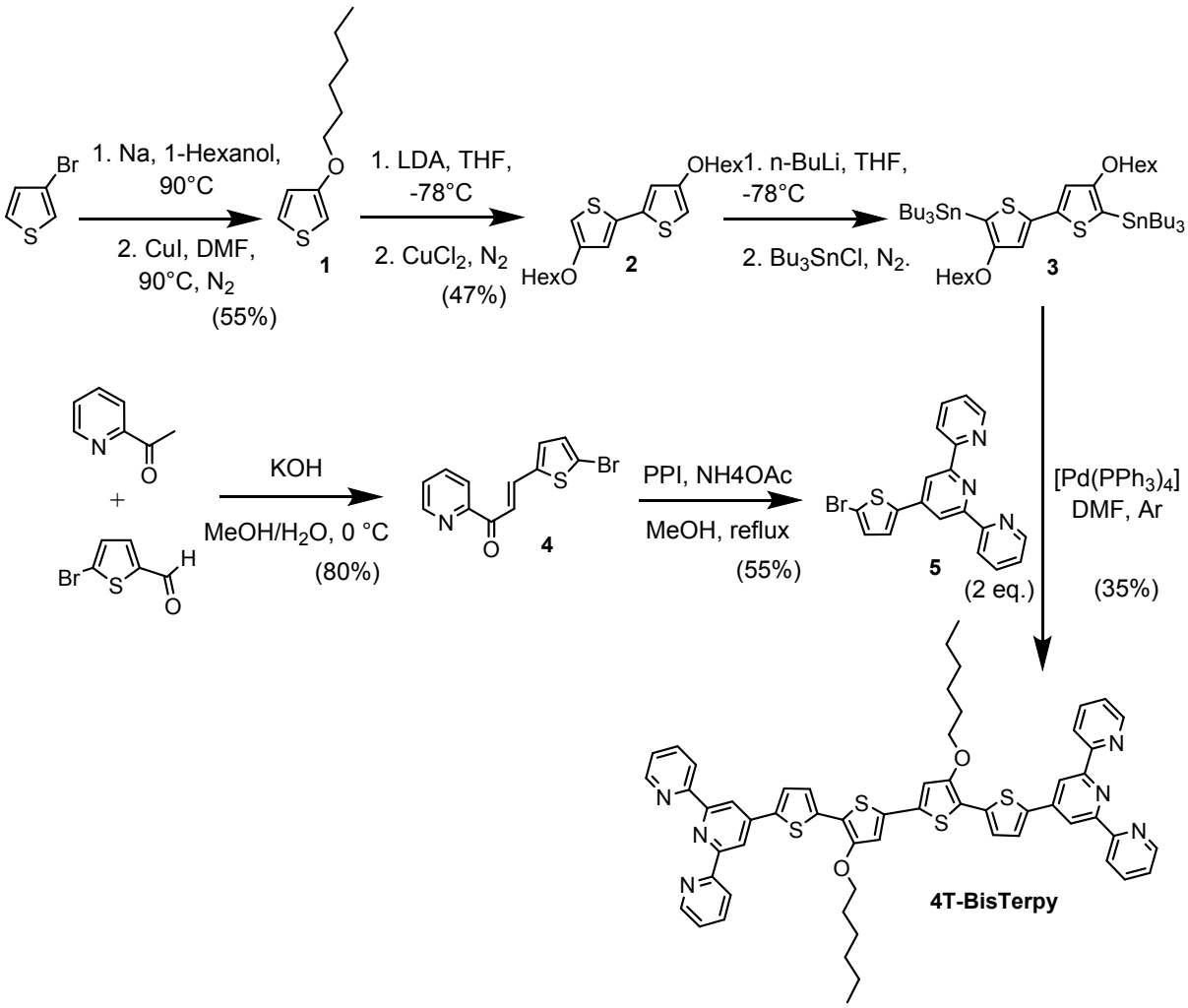
SUPPORTING INFORMATION

Synthesis:

The targeted compound **4'-(3',4''-Dihexyloxy-5,2':5',2'':5'',2'''-quaterthien-2,5'''-diyl)-bis(2,2':6',2''-terpyridine)** (**4T-BisTerpy**) was synthesized in 6 steps according the synthetic pathway described hereafter. 3-bromothiophene was converted to 3-hexyloxythiophene (**1**) in the presence of sodium hexanoate and CuI. Then, compound **1** was treated first with LDA and coupled with copper iodide to give 2,2'-bi(4-hexyloxythiophene) (**2**). Dilithiation of the bi-thiophene derivative with butyl lithium and reaction with tributyltin chloride afforded the bis(tributylstannyl) derivative **3**. The 4'-(5-Bromo-2-thienyl)-2,2':6',2''-terpyridine (**5**) was synthesized according to the Kröhnke's method. A Stille coupling between two equivalent of bromo derivative (**5**) and the bis-stannyl derivative (**3**) in the presence of palladium catalyst leads to **4T-BisTerpy**.



Synthetic pathway of **4T-BisTerpy**

Experimental Section

Characterization techniques:

NMR spectra were recorded with a Bruker AVANCE AC 200 MHz (^{1}H, 200.13 MHz and ^{13}C, 50.32 MHz). Chemical shifts are given in ppm relative to TMS. UV-Vis spectra were recorded with a Perkin Elmer paragon 500 spectrometer with Bio-Tek UVIKON XS spectrometer. Electrospray mass spectra (MS-ESI) were acquired in the positive mode on a LCQ-ion trap Thermofinnigan spectrometer equipped with an electrospray source and fast atom bombardment mass spectra (MS-FAB) were recorded with a AIE Kratos MS 50 mass spectrometer fitted with an Ion Tech Ltd gun. A standard FAB source was used and m-nitrobenzylalcohol (NBA) was the liquid matrix. Elemental analyses were carried out by the Analytical Service of CNRS Vernaison.

Reagents and chemicals

All reagents and chemicals were purchased from Aldrich. Reagents and chemicals were used as received until it was mentionned.

3-Hexyloxythiophene (1). In a three neck under argon atmosphere, sodium (1.88 g, 82 mmol) was charged to 1-Hexanol (35 mL). This mixture was heated at 90°C until no metal sodium left. Then, hexanol excess was removed with vacuum distillation to get the sodium hexanoate. 3-Bromothiophene (12 g, 73.6 mmol) and CuI (2.6 g, 13.6 mmol) was added to the white solid obtained previously dissolved in dry DMF (40 mL). The mixture was heated overnight at 90°C under argon. Afterward, water (100 mL) was added and the aquous phase was extracted with Hexane. The organic phases were gathered together, washed with water, dried (Na_2SO_4) and concentrated. The purification was realized by vacuum distillation (0.1 mm of Hg), the first fraction was the excess of hexanol and the second fraction gave **1** (80°C at 1 mm of Hg) as colorless oil (7.5 g, 55 %). ^{1}H NMR ($CDCl_3$) : δ = 7.16 (dd, 1H, ^3J = 5.2 Hz, ^4J = 3.0 Hz), 6.75 (dd, 1H, ^3J = 5.2 Hz, ^4J = 1.5 Hz), 6.22 (dd, 1H, ^4J = 3.0 Hz, ^4J = 1.5 Hz), 3.94 (t, 2H, ^3J = 6.4 Hz), 1.77 (qu, 2H, ^3J = 6.4 Hz), 1.50 – 1.20 (m, 6H), 0.90 (t, 3H, ^3J = 6.2 Hz).

2,2'-Bi(4-hexyloxythiophene) (2). A LDA solution prepared with n-Butyllithium (3.2 mL, 2.5 M in hexane, 8 mmol) added dropwise to a stirred solution of diisopropylamine (1.15 mL, 8.14 mmol) in dry THF (5 mL) under argon at 0°C was cannulated to a solution of **1** (1.5 g, 8.14 mmol) in dry THF (20 mL) at – 78°C under inert atmosphere. This mixture was stirred 1 H at this tempetraure then $CuCl_2$ solid was added and the solution warmed to room temperature. After 12H of stirring, water (50 mL) and diethyl ether was added. The organic phase was separated by decantation and the aqueous phase was extracted two more times with diethyl ether. The organics phases were collected, sewpt through celite, dried (Na_2SO_4) and concentrated. Chromatography on silica gel (1:9 CH_2Cl_2/petroleum ether) gave **2** as a yellow solid (650 mg, 47%). ^{1}H NMR ($CDCl_3$) : δ = 6.81 (d, 2H, ^4J = 1.8 Hz), 6.10 (d, 2H, ^4J = 1.8 Hz), 3.92 (t, 4H, ^3J = 6.5 Hz), 1.76 (qu, 4H, ^3J = 6.3 Hz), 1.50 – 1.20 (m, 12H), 0.91 (t, 6H, ^3J = 6.4 Hz).

(*E*)-3-(5-Bromo-2-thienyl)-1-(2-pyridyl)prop-2-en-1-one (4). KOH (2.94 g, 52.3 mmol) was dissolved in a mixture of methanol and water (5:1, 120 mL) and cooled to 0 °C. Afterward, 3-bromothiophene-2-carboxaldehyde (10 g, 52.3 mmol) and 2-

acetylpyridyne (6.34 g, 52.3 mmol) were charged successively and the mixture was stirred 3 H at 0 °C. The formed precipitate was filtered and washed with cold methanol to get **4** as yellow-green solid (15.4 g, 80 %). ^{1}H NMR ($CDCl_3$) : δ = 8.72 (ddd, 2H, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz), 8.15 (ddd, 2H, ^3J = 7.6 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz), 7.98 (d, 1H, ^3J = 15.8 Hz), 7.88 (d, 1H, ^3J = 15.8 Hz), 7.86 (td, 2H, ^3J = 7.6 Hz, ^4J = 1.8 Hz), 7.48 (ddd, 2H, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz), 7.13 (d, 1H, ^3J = 3.9 Hz), 7.04 (d, 1H, ^3J = 3.9 Hz).

4'-(5-Bromo-2-thienyl)-2,2':6',2''-terpyridine (5). 1 (2.94 g, 10 mmol), Pyridacyl pyridinium iodide (3.26 g, 10 mmol) and NH_4OAc (771 mg, 10 mmol) were refluxed in methanol under Argon. After 6 H, the precipitate obtained was filtered and the methanol solution was refluxed again. After 6 H, the new precipitate was filtered again. This was repeated until no more precipitate appeared. The grey precipitates were gathered together and washed with cold methanol and filtered on alumina plug (eluent: $CHCl_3$) to give **5** as a white solid (2.1 g, 53 %). m.p.= 224 – 226 °C. ^{1}H NMR ($CDCl_3$) : δ = 8.72 (ddd, 2H, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz), 8.62 (ddd, 2H, ^3J = 7.5 Hz, ^4J = 1.0 Hz, ^5J = 0.9 Hz), 8.59 (s, 2H), 7.87 (td, 2H, ^3J = 7.5 Hz, ^4J = 1.8 Hz), 7.51 (d, 1H, ^3J = 4.0 Hz), 7.35 (ddd, 2H, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz), 7.11 (d, 1H, ^3J = 4.0 Hz). UV/Vis (CH_2Cl_2) : λ = 288 nm (log ε = 4.59) ; 311 (sh).

4'-(3',4''-Dihexyloxy-5,2':5',2'':5'',2'''-quaterthien-2,5'''-diyl)-bis(2,2':6',2''-terpyridine) (4T-BisTerpy). A solution of n-BuLi 2.5 M in hexane (1 mL, 2.2 eq.) was added dropwise to a solution of **2** (500 mg, 1.36 mmol) in anhydrous THF (10 mL) under Ar at room temperature. After 30 min of stirring, Bu_3SnCl (0.9 mL, 2.4 eq.) was slowly added and the reaction mixture was stirred for 1 h at 30°C. After dilution with CH_2Cl_2 (60 mL), the organic phase was successively washed with a satured aqueous solution of NH_4Cl and water, dried over Na_2SO_4 and evaporated in vacuo. The 5,5'-Bis(tributylstannyl)-2,2'-bi(4-hexyloxythiophene) (**3**) obtained was directly used in the following step without further purification. A mixture of **3** (1.1 g, 1.16 mmol), **5** (1 g, 2.2 eq.) and $Pd(PPh_3)_4$ (156 mg, 0.1 eq.) in anhydrous DMF (10 mL) was heated overnight at 100°C under a Ar atmosphere. Then, water was added to the mixture to get brown solid which was filtered, washed with water, methanol and diethyl ether. Afterward the solid was dissolved in hot $CHCl_3$ and filtered on alumina plug ($CHCl_3$ then $CHCl_3$/THF (9:1)) to get **4T-BisTerpy** as purple solid (400 mg, 35%). m.p. > 250°C, ^{1}H NMR ($CDCl_2$-$CDCl_2$) : δ = 8.72 (d, 4H, ^3J = 3.8 Hz), 8.63 (s, 4H), 8.60 (d, 4H, ^3J = 7.0 Hz), 7.88 (t, 4H, ^3J = 7.0 Hz), 7.71 (d, 2H, ^3J = 3.8 Hz), 7.36 (dd, 4H, ^3J = 7.0 Hz, ^3J = 3.8 Hz), 7.28 (d, 2H, ^3J = 3.8

Hz), 6.96 (s, 2H), 4.21 (t, 4H, ^3J = 6.2 Hz), 1.92 (qu, 4H, ^3J = 6.4 Hz), 1.75 – 1.27 (m, 12H), 0.90 (t, 6H, ^3J = 6.6 Hz). ^{13}C NMR ($CDCl_2$-$CDCl_2$) : δ = 157.5, 155.1, 150.8, 144.8, 140.6, 138.5, 136.7, 134.5, 127.9, 125.3, 125.2, 122.9, 118.1, 115.9, 114.7, 73.9, 33.2, 31.2, 27.4, 24.2, 15.8. UV/Vis (CH_2Cl_2) : λ = 479 (log ε = 4.74), λ = 278 (log ε = 4.65). ESI-MS m/z : 993 $[M + H]^+$. Anal. for $C_{58}H_{52}O_2N_6S_4$ (calcd) : C 70.11 (70.13) H 5.62 (5.28), N 7.96 (8.46), S 12.51 (12.91).

STM characterization:

Molecular alkyl chains:

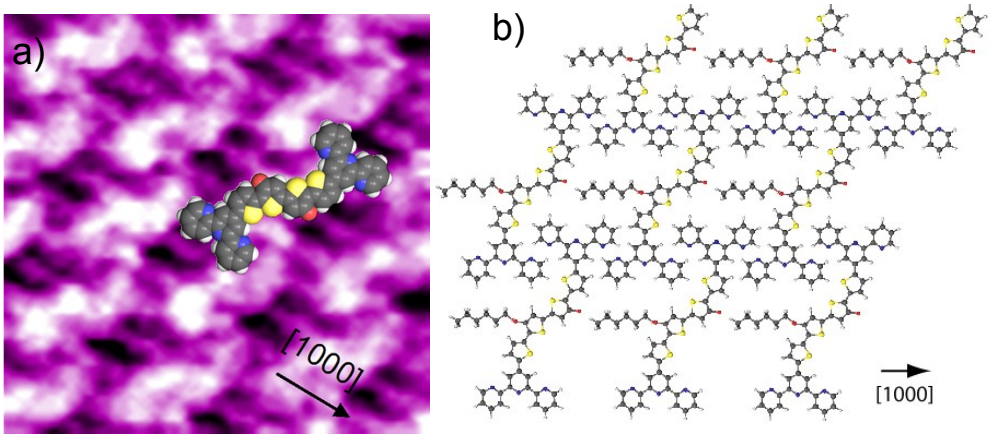


Figure S1: (a) STM images of the molecular domain. Molecular alkyl chains can be observed in the conjugated network cavities, 7x7 nm², V_s=0.55 V, I_t = 9 pA. (b) Model.

Molecular alkyl chains are rarely observed in the STM images. This therefore suggests that molecular alkyl chains are usually not adsorbed on the surface. In fig.S1 is presented a rare STM image where some of the molecular alkyl chains can be observed. The Fig.S1 shows that the molecular alkyl chains are laying on the graphite surface (along the [1000] graphite orientation) in the network cavities.