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Regiospecifity-driven self-assembly of methyl substituted quaterthiophenes at surface

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ABSTRACT

A study on the self-assembly of regiochemically differentiated methyl substituted quaterthiophenes is presented. Hierarchical self-assembly of 5,4′,3″,5‴-tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene molecule, **7** leads to unprecedented fluorescent superstructures on glass and mica surfaces made by reiteration of a peculiar V-shaped recurring motif that extended at least for three generations.

1. Introduction

Oligothiophenes are widely investigated as active components for several applications, such as optics and molecular electronics [1,2]. Information on the spatial arrangement of the molecules at mesoscale in solid films is essential for the understanding of the final device performances [3,4]. Although proper methods for the thin films growth are indispensable [5,6], strategic molecular engineering and efficient synthetic procedures are key elements [7].

It has been shown that the size of alkyl end substituents (generally C2–C6 chains) is not the only parameter affecting the self-organization of oligothiophenes at surface [8]. In fact, both of differences in size of alkyl and perfluoroalkyl chains and regiochemistry of thiophene substitution may dramatically alter the whole solid state features of the oligomers [9,10].

Quaterthiophene (T4) is among the most investigated organic semiconductors [1]. We explore here a study on the effect of tailored methyl substitution on the self-organization of T4 semiconductors both at molecular and meso-scale level. It's worth to mention, in fibrils forming polyaniline, that the insertion of meta methyl substituents in the phenyl ring, leads to helicity inversion of the nanofibers at the surface, both at molecular and supramolecular levels [11].

We show that from amorphous films to fibrillar superstructures to crystalline platelets can be achieved on glass substrate by self-assembly of tailored methyl substituted T4.

2. Experimental details

Microwave (MW) experiment were carried out in a Milestone Microsynth Labstation operating at 2450 MHz monitored by a proprietary control unit. The oven was equipped with magnetic stirring, pressure and temperature sensors. Reactions were performed in a glass vessel (capacity 10 mL) sealed with a septum. The MW method was power controlled (100 W maximum power input) and the samples were irradiated with the required power output (setting at the maximum power) to achieve the desired temperature (80 °C). All Proton Nuclear Magnetic Resonance (^{1}H NMR) and Carbon Nuclear Magnetic Resonance (^{13}C NMR) spectra were recorded at room temperature on a Varian Mercury-400 spectrometer equipped with a 5-mm probe (spectra reported as Supporting Information). UV–Vis spectra were recorded using a Perkin Elmer Lambda 20 spectrometer. Photoluminescence spectra were collected on a Perkin Elmer LS50 spectrofluorometer. Fluorescence measurements were performed using an excitation wavelength corresponding to the maximum absorption lamda. Melting points were determined on Kofler bank apparatus and are uncorrected. Flash chromatographies were carried out using silica gel (200–300 mesh ASTM). Analytical thin layer cromatographies were carried out using 0.2 mm sheets of silica gel 60

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F_{254} and the visualization accomplished by UV lights (356 nm and 254 nm).

SATCAT Pd-catalyst used in this work was prepared following the already reported procedures [12,13], obtaining a Pd loading of about 0.2 mmol g^{-1} as confirmed by Inductively Coupled Plasma analysis. Diffuse Reflectance IR analysis of the materials showed a diagnostic peak at 1638 cm^{-1} due to the formation of the pyridylimine unit.

Compounds **2** and **6** were prepared following already described procedures by metallation through *n*-BuLi 2.5 M and quenching by 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane at −78 °C in Et_2O [14]. The characterization of *4,4,5,5-tetramethyl-2-(4-methyl-thiophen-2-yl)-[1,3,2]dioxaborolane,* **4** has already been reported [15].

2.1. General procedure for SATCAT catalyzed Suzuki reaction for the preparation of methyl substituted quarterthiophenes

The MW oven reactor was charged with 50 mg of di-iodo derivative **1** (0.112 mmol), 75 mg of the desired boro-derivative (0.336 mmol), 26 mg of KF (0,448 mmol), 56 mg of SATCAT (0.0112 mmol) and 2 mL of isopropanol. The reaction mixture was irradiated under stirring for 50 min at $T = 80$ °C and $P = 100$ W. The solvent was removed under reduced pressure, and the crude products were purified by chromatography (silica gel, petroleum ether/ethyl acetate 100:0 to 90:10). The analytical data for the specific compounds are given below.

3,4′,3″,3‴-tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, **3.** Amorphous bright yellow solid (75% yield). ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.11 (d, $^3J = 5.1$ Hz, 2H), 6.97 (s, 2H), 6.87 (d, $^3J = 5.1$ Hz, 2H), 2.41 (s, 6H), and 2.23 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 136.82, 136.08, 133.87, 131.44, 130.97, 128.85, 128.35, 123.14, 15.44, and 14.94. MS (70 eV, EI): *m/z* 386 (M^+). Anal. calcd for $C_{20}H_{18}S_4$ (386.62): C, 62.13; H, 4.69. Found: C, 62.19; H, 4.75.

4,4′,3″,4‴-tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, **5:** Microcrystalline bright yellow-orange solid (78% yield). ^1H NMR (CD_2Cl_2, TMS/ppm) δ 7.00 (s, 2H), 6.99 (broad s, 2H), 6.81 (m, 2H), 2.24 (broad s, 6H), and 2.18 (s, 6H); ^{13}C NMR (CD_2Cl_2, TMS/ppm) δ 139.09, 137.89, 137.25, 137.11, 128.24, 126.89, 126.31, 120.20, 15.80, and 15.14. MS (70 eV, EI): *m/z* 386 (M^+). Anal. calcd for $C_{20}H_{18}S_4$ (386.62): C, 62.13; H, 4.69. Found: C, 62.05 H, 4.64.

5,4′,3″,5‴-tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, **7:** Amorphous yellow ocher solid (82% yield). ^1H NMR ($CDCl_3$, TMS/ppm) δ 6.92 (m, 2H), 6.91 (s, 2H), 6.64 (m, 2H), 2.46 (broad s, 6H), and 2.18 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 139.17, 137.13, 137.04, 134.90, 127.59, 126.03, 125.98, 123.44, 15.35, and 14.98. MS (70 eV, EI): *m/z* 386 (M^+). Anal. calcd for $C_{20}H_{18}S_4$ (386.62): C, 62.13; H, 4.69. Found: C, 62.21; H, 4.77.

4,4,5,5-tetramethyl-2-(3-methyl-thiophen-2-yl)-[1,3,2]dioxaborolane, **2.** ^1H NMR ($CDCl_3$, TMS/ppm) δ 1.33 (s, 12H), 2.53 (s, 3H), 6.84 (m, 1H), and 7.45 (m, 1H). MS (70 eV, EI): *m/z* 224 (M^{+1}).

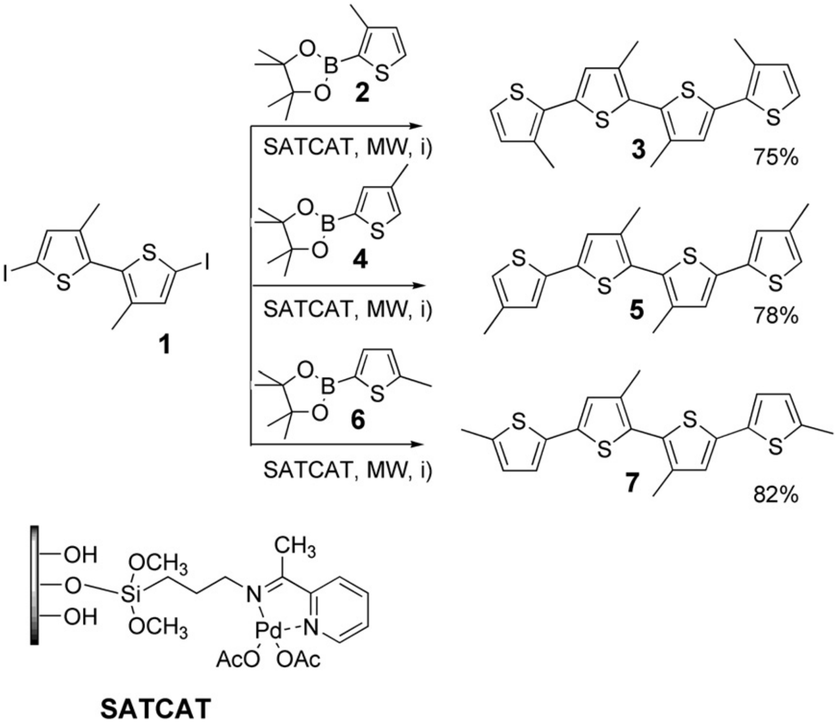
4,4,5,5-tetramethyl-2-(5-methyl-thiophen-2-yl)-[1,3,2]dioxaborolane, **6.** ^1H NMR ($CDCl_3$, TMS/ppm) δ 1.34 (s, 12H), 2.49 (s, 3H), 6.98 (d, 1H, $J = 4.4$ Hz), and 7.48 (d, 1H, $J = 4.8$ Hz). MS (70 eV, EI): *m/z* 224 (M^{+1}).

2.2. X-ray diffraction (XRD)

Thin films XRD measurements were carried out at room temperature with a Bragg/Brentano diffractometer (X'pertPro Panalytical) equipped with a fast X'Celerator detector, using Cu anode as X-ray source (Kα, $\lambda = 1.5418$ Å). The simulated X-ray diffraction pattern was obtained by using the PowderCell program [16].

Data for **7** were collected on a a Bruker SMART Apex II CCD diffractometer; data reduction, solution and refinement (on F^2(obs)) used the programs SMART, SAINT [17], SIR97 [18] and SHELXTL [19]. Molecular graphics were generated using Mercury v. 2.0 [20] and SCHAKAL99 [21].

$C_{20}H_{18}S_4$, $M = 386.62$, monoclinic, space group $P2_1/c$; $a = 12.496(14)$, $b = 14.267(16)$, $c = 11.515(13)$ Å, $\beta = 115.518(12)°$; $U = 1853(4)$ Å^3, $T = 293(2)$ K; $Z = 4$, μ(Mo-Kα) $= 0.512$ mm^{-1}, $Dc = 1.386$ g cm^{-3}, F(000) = 808, 8509 reflections collected. Refinement of 2407 unique reflections ($R_{int} = 0.1106$) converged at a final $R_1 = 0.0826$ ($I > 2\sigma(I)$) and $wR_2 = 0.2542$ (all data), GOF = 0.98.



Scheme 1. Synthetic route to methyl substituted quaterthiophenes **3**, **5** and **7** namely 3,4′,3″,3‴-tetramethyl/4,4′,3″,4‴-tetramethyl and 5,4′,3″,5‴-tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, respectively. i) SATCAT, isopropanol, KF, MW, 80 °C, 50′.