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Synthesis and Supramolecular Organization of Regioregular Polythiophene Block Oligomers

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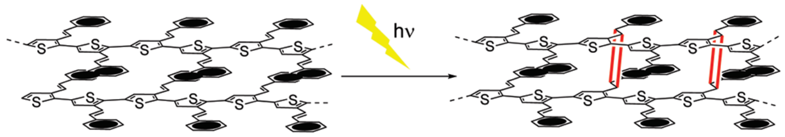

The self-assembly of functional polythiophenes was studied by a bottom-up approach "from molecule to polymer". The synthesis and the X-ray structure of 2,5-dibromo-3-styryl and 3-2′,3′,4′,5′,6′-pentafluorostyryl-thiophenes revealed a supramolecular arrangement controlled by $\pi-\pi$ interactions between the aromatic rings. A [2 + 2] photocyclization reaction in the solid state of (*E*)-1-2′,5′-dibromo-3′-thienyl-2-pentafluorophenylethene triggers the formation of a rare cycloadduct comprising thiophene rings. The X-ray analysis confirmed its *rctt* stereochemistry. The synthesis of P3HT-*b*-P3ST and P3HT-*b*-P3STF block oligomers was achieved by a GRIM method in good yields. An indirect proof of well-defined nanostructured organization was provided by the partial photocyclization of pendant styryl moieties under UV irradiation.

Introduction

Engineering of advanced materials at the micro- and nanoscale is a permanent requirement for the construction of next-generation polymer nanodevices. In this regard, the microfabrication of integrated circuits is mainly ensured by photolithography, this conventional method consisting in the transfer of a geometric shape from a photomask to a light-sensitive compound. Over the past decades, lithographic techniques have dramatically enhanced the pattern resolution and reached an unprecedented degree of miniaturization down to 30−40 nm.[1] However, efforts toward further downscaling are time-consuming and might limit the future developments of photolithography and related methods. Thus, the "bottom-up" approach has arisen as a rational alternative to the economic and technological challenges faced by the semiconductor industry.[2] The design of tridimensional structures could afford new successful pathways via the accurate scaling of polymer nanodevices.

During the past few years, π-conjugated polymers and more specifically polythiophenes have attracted tremendous interest, stimulated by their potential applications in the development of new systems such as light-emitting diodes (LEDs), electrochromic displays, field-effect transistors (FETs), and more recently, photovoltaic devices.[3] The performance of

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these semiconducting materials is closely related to the electronic interactions between the polymer chains in the solid state, which in turn depends on their supramolecular organization.[4] Indeed, the combination of well-ordered π-conjugated structures and a homogeneous domain distribution is required for the formation of highly efficient electronic devices at the macroscopic level. Thus, the rational design of starting building blocks should impart a highly ordered pattern to the functional macromolecular organization by a bottom-up control. Consequently, this process should significantly improve the physical properties of new organic electronic materials. In this context, the supramolecular concept offers new alternatives for the engineering of such systems and their integration into cost-effective processes.

The advent of supramolecular chemistry has opened new perspectives for the fabrication of such functional materials.[5] A wide variety of intermolecular noncovalent interactions ($\pi-\pi$ stacking, hydrogen bonding, halogen bonding, or metal–ligand coordination) has emerged in the supramolecular toolbox and represents diverse options at the chemist's disposal.[6] Extension of these supramolecular concepts to polymeric materials leads to their self-assembly into controlled supramolecular architectures through recognition processes.[7] Block copolymers are well-known examples of self-assembling systems, which rely upon microphase separation of chemically distinct blocks into nanoscale periodic domains.[8] The resulting arrangements depend on the relative length and incompatibility of the polymer blocks, the connectivity constraints, and the type of interactions.

In the quest for high performance organic materials, the engineering of well-organized nanodevices is thereby under development in numerous research groups. In this contribution, we present the synthesis of 2,5-dibromo-3-styrylthiophene and 1-2′,5′-dibromo-3′-thienyl-2-pentafluorophenylethene and their organization at the molecular scale. $\pi-\pi$ interactions between aromatic rings exert a high level of control over the crystalline arrangement, which is illustrated by the conversion of (*E*)-1-2′,5′-dibromo-3′-thienyl-2-pentafluorophenylethene into the corresponding cycloadduct by a [2 + 2] photocyclization reaction in the solid state. Subsequent polymerizations between the 3-hexylthiophene and styrylthiophene derivatives have been carried out by the Grignard metathesis (GRIM) methodology. GRIM is a synthesis method for regioregular aromatic polymers recently developed by McCullough et al.[9] and further modified by Yokozawa et al.[10] One interesting feature of GRIM is its quasi-living chain growth mechanism,[11] which could lead to the possibility of developing a regioregular block copolymer with a narrow PDI in one pot. In this study, well-defined diblock structures with self-complementary cores, i.e., poly(3-hexylthiophene)-*b*-poly(3-styrylthiophene) (P3HT-*b*-P3ST) and poly(3-hexylthiophene)-*b*-poly(3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene) (P3HT-*b*-P3STF), were synthesized via GRIM polymerization. The incorporation of poly(3-hexylthiophene) (P3HT) blocks is motivated by its remarkable physical properties, namely, a high hole-mobility supplemented by a high solubility in a variety of organic solvents. These properties have been associated with their molecular organization in the solid state. Recently, similar π-stacked molecular assemblies have been reported for polythiophene with acetylenic side chains or π central systems (fused thiophene, pyridazine, etc.) leading to a hole mobility larger than that of P3HT.[12] On the basis of these findings, our block oligomers with the pendant styryl moieties should exhibit a strong tendency to form a π-stacked molecular arrangement. This effective supramolecular organization of block oligomers P3HT-*b*-P3ST and P3HT-*b*-P3STF by $\pi-\pi$ stacking is demonstrated by concomitant covalent bond formation under UV irradiation in the solid state, this strategy providing an indirect evidence of well-ordered structures.

Results and Discussion

Synthesis of the Monomers. 3-Styrylthiophene monomers **2** and **3** were synthesized according to conventional synthetic routes as illustrated in Scheme 1. A Wittig reaction between 2,5-dibromo-3-thiophenecarboxaldehyde **1** and benzyltriphenylphosphonium bromide in the presence of DBU provides 2,5-dibromo-3-styrylthiophene **2** as a mixture 1.5:1 of E/Z isomers (Scheme 1).[13]

The amount of Z isomer was determined by ^{1}H NMR spectroscopy by integration of peaks at 6.69 and 6.33 ppm ($^3J_{H-H}$ = 12.0 Hz) assigned to the vinylic protons of the *cis* isomer, with respect to the doublets at 7.00 and 6.89 ppm ($^3J_{H-H}$ = 16.5 Hz) for the *trans* double bond. Subsequent treatment with iodine for 7 days at room temperature allowed the isomerization into the (*E*)-2,5-dibromo-3-styrylthiophene **2**. However, the presence of a residual amount of Z isomer (95:5 conversion ratio of *E*/*Z* olefins **2**) required a further purification by chromatography to give the (*E*)-isomer **2** in pure form (Figures S4 and S5 in Supporting Information). For the fluorinated monomer **3**, perfluorobenzyltriphenylphosphonium bromide was used as Wittig

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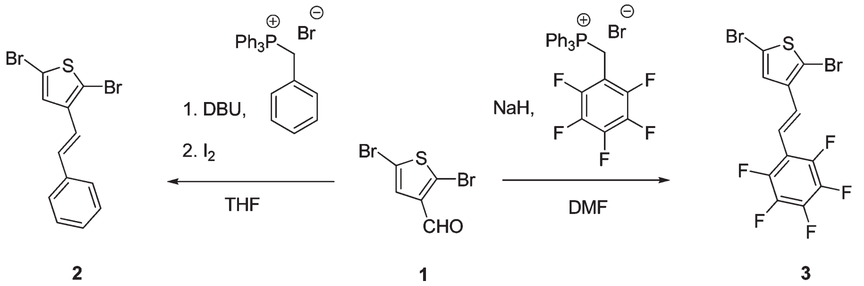
SCHEME 1. Synthesis of 3-Styryl Monomers 2 and 3



reagent. When 2,5-dibromo-3-thiophenecarboxaldehyde **1** reacted with the phosphonium salt in the presence of sodium hydride, the (*E*)-1-2′,5′-dibromo-3′-thienyl-2-pentafluorophenylethene **3** was formed in 78% yield as a single isomer.

The facile crystallization of compounds **2** and **3** convinced us to study their crystal packing by single crystal X-ray diffraction. The crystallographic data of (*E*)-2,5-dibromo-3-styrylthiophene **2** revealed a nearly planar conformation; the thiophene and phenyl rings are slightly rotated relative to each other by an angle of 4.5(2)°.

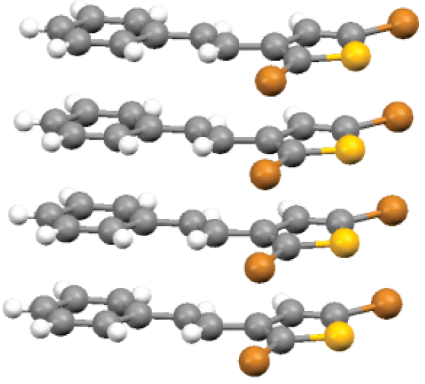


FIGURE 1. Columnar arrangement in a head-to-head mode of compound **2**. Colors are as follows: gray, carbon; white, hydrogen; brown, bromine; orange, sulfur atoms.

From the supramolecular point of view, the small difference in polarity combined with the large difference in width of the two aromatic groups induces a columnar organization in a head-to-head fashion in the crystals of **2** dominated by $\pi-\pi$ interactions, as shown in Figure 1. The efficient $\pi-\pi$ stacking leads to a close parallel packing of the olefins with a repeat intermolecular distance between the double bond centers of 3.94 Å. Moreover, Br$\cdots$S intermolecular distances of 3.82 Å are also observed and contribute to the stabilization of the supramolecular scaffold.

Interestingly, the centroid-centroid separation between the phenyl and thiophene rings is exactly the same (3.94 Å), which confirms the perfect superposition of successive molecules. A second relevant feature lies in an unusual supramolecular arrangement, namely, a noncentrosymmetric order and macroscopic polarity; adjacent molecular columns adopt a nearly perpendicular orientation in herringbone geometry (Figure 2).

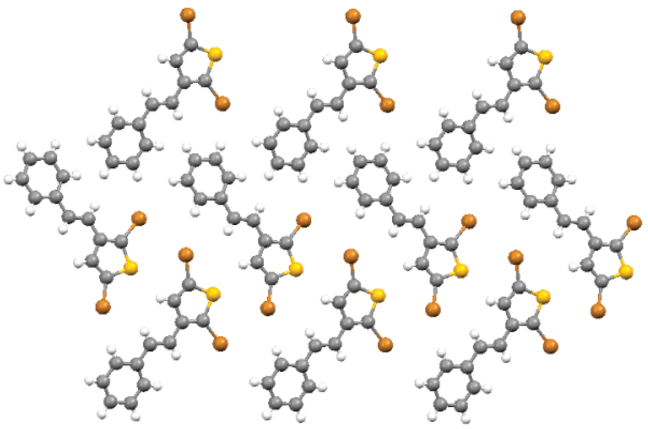


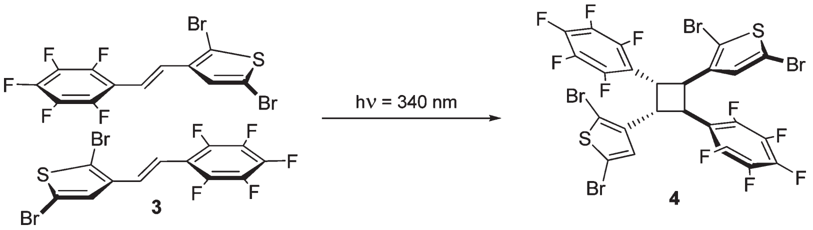
FIGURE 2. View down the crystallographic *a* axis of the noncentrosymmetric organization of compound **2**. Colors are as follows: gray, carbon; white, hydrogren; brown, bromine; orange, sulfur atoms.

In (*E*)-1-2′,5′-dibromo-3′-thienyl-2-pentafluorophenylethene **3**, the presence of the perfluorinated ring was expected to change the supramolecular organization dramatically. Indeed, it is well-established that pentafluoroaromatic groups possess an opposite dipole moment with respect to their hydrogenated counterparts, and consequently the molecules self-assemble through strong π-donor/π-acceptor interactions. The slow evaporation of a chloroform solution of compound **3** provides suitable material for a single crystal X-ray analysis. The molecules are almost planar (3.1(1)° between the aromatic rings) and the stronger $\pi-\pi$ interactions between the thiophene and pentafluorophenyl groups, as well as the smaller difference in width between the two groups as compared to **2**, now pairs the molecules in a head-to-tail mode. At the supramolecular level, the pairs of molecules again stack in columns with distances between double bond centers of 3.646(3) Å within pairs and 3.733(3) Å between pairs (Figure 3). This supramolecular arrangement is well illustrated in the molecular packing diagram of **3** in Supporting Information (Figure S6).

This arrangement results in a packing that is similar to that of **2** with every second molecule in the columns inverted, leading to the space group $P21/c$. In this structure, a number of contacts shorter than the van der Waals radii exist (i.e., two F$\cdots$Br intermolecular distances of 3.22 and 3.33 Å), indicating both the strength of the $\pi-\pi$ interactions and the less ideal fit of the molecules in the plane due to the larger size of the fluorinated ring.

Thus, supramolecular scaffolds formed by the thiophene units **2** and **3** confirm their effective association owing to $\pi-\pi$ interactions. The incorporation of styrylthiophene units in the oligomer backbone is thereby expected to be a reliable approach for controlling the self-assembly of oligomers via π-stacked groups. Moreover, the introduction

SCHEME 2. **Photocyclization Reaction in the Solid State of Olefin 3**



of well-adjusted pending double bonds along the oligomeric chain represents an original strategy to lock the system through covalent bond formation mediated by photoirradiation. This methodology would ensure a fine supramolecular control of the architecture and prevent any segregation of block co-oligomers.

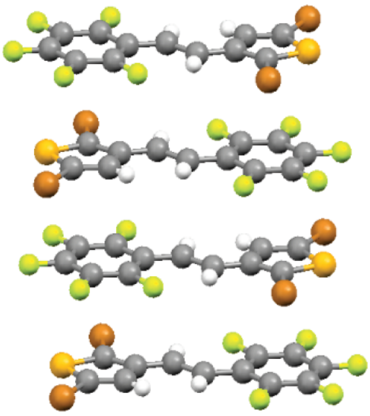


FIGURE 3. Columnar arrangement in a head-to-tail fashion of compound **3**. Colors are as follows: gray, carbon; white, hydrogen; brown, bromine; yellow, fluorine; orange, sulfur atoms.

Photodimerization. The [2 + 2] photocyclization reaction in the solid state represents a distinctive mode of covalent bond formation in a regio- and stereoselective manner.[14] This solventless approach affords highly valuable products in high yields with low impact on the environment, also as a result of the reduced formation of byproducts. Specific geometric criteria postulated by Schmidt have outlined the requirements that two double bonds should meet for undergoing such a reaction,[15] and further investigations have depicted the topochemical principles for evaluating the possible occurrence of such dimerizations.[16] Thus, a pair of olefinic bonds should be arranged approximately parallel to one another at a distance in the range of 3.5−4.2 Å, as observed in compounds **2** and **3**. Interestingly, $\pi-\pi$ interactions occurring between a pair of aromatic rings have found some applications as a driving force for potentially photoreactive structures.[17] This functional aspect lies in the distance between the π-stacked groups, which fits with the topochemical postulate, i.e., a typical cutoff distance of 3.9 Å.[18]

As mentioned before, the structural organization of styrylthiophene derivatives **2** and **3** exhibits a distance between the double bonds of less than 4.2 Å, which fits the requirement of Schmidt's rules (i.e., 3.94 Å in sample **2**, 3.65 and 3.73 Å in sample **3**). Accordingly, it has been decided to study the ability of olefin **3** to undergo a [2 + 2] cycloaddition reaction in the solid state under UV irradiation. Finely powdered crystals of **3** were placed between two glass plates and photoirradiated with a UV lamp at 340 nm for 24 h (Scheme 2).

The ^{1}H NMR analysis of the resulting yellowish powder has revealed unequivocally a nearly quantitative photocyclization by the vanishing of the peaks initially present at 7.32 and 6.77 ppm and the appearance of a new peak at 4.81 ppm corresponding to the cyclobutane protons (Figure 4).[19] This unique signal confirmed the creation of one single stereoisomer **4** with the cis, trans, trans (*rctt*) geometry.

X-ray diffraction analysis of a single crystal of cycloadduct **4** (grown by slow evaporation of a $CHCl_3$ solution) has provided a clear confirmation of the *rctt* arrangement of the cyclobutane ring, according to the topochemical expectation for the *E* isomer of the carbon−carbon double bond. Consistent with this geometry, the pairs of pentafluorobenzene and thiophene groups point to opposite directions with respect to the plane of the cyclobutane ring (Figure 5).

Five H···F intramolecular contacts involving the fluorine atoms in ortho position of the pentafluorobenzene group and hydrogen atoms belonging to the cyclobutane ring, namely, H6···F9 (2.35 Å), H7···F13 (2.40 Å), H27···F35 (2.33 Å), H27···F9 (2.44 Å), and H26···F29 (2.53 Å), are observed. This peculiar conformation of the molecule results in a dumbbell shape that is notoriously difficult to pack. As a result, shape requirements take precedence, and no $\pi-\pi$ interactions between the thiophene and pentafluorophenyl rings are observed; a sharp contrast with respect to the starting building block **3**. The molecular packing diagram of **4** is provided for comparison with **3** in Supporting Information (Figure S7). To the best of our knowledge, this resulting 4,4′-[(1α,2α,3β,4β)-1,3-bis(2,5-dibromo-3-thienyl)-2,4-bis(pentafluoro-phenyl)]cyclobutane **4** is the first 3-thiophene-substituted cyclobutane reported to date and constitutes a very rare type of cyclobutane derivative containing a thiophene heterocycle.[20]

For monomer **2**, UV irradiation was performed under the same conditions. After 24 h, the white compound **2** turned brown but the crystalline morphology remained consistent. The ^{1}H NMR analysis of the crude material confirms a

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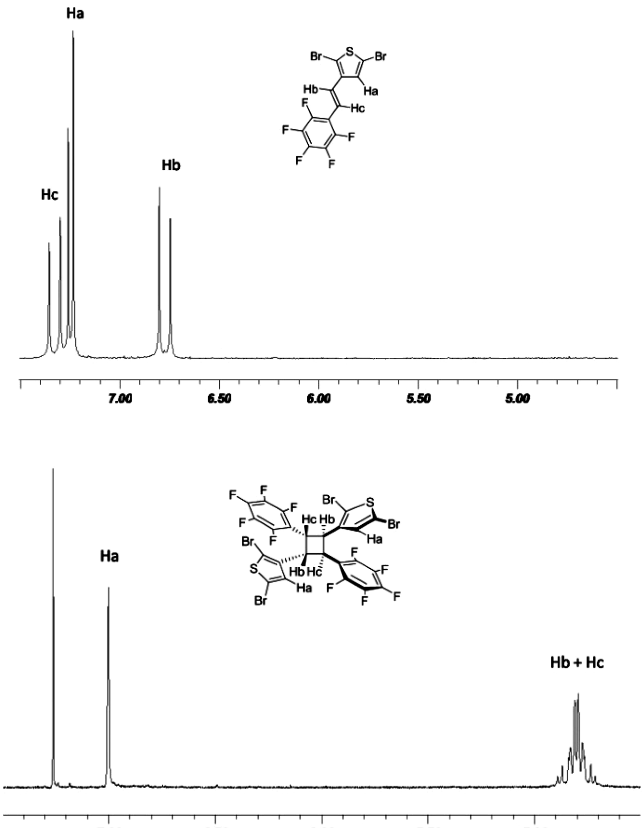

FIGURE 4. ^{1}H NMR spectra of olefin **3** (upper) and cycloadduct **4** (lower) in CDCl$_3$ at room temperature.

cycloaddition reaction by the appearance of a peak at 4.4 ppm (cyclobutane protons), but the photoreactive olefin **2** was converted into the corresponding cycloadduct in low yields (about 20%, determined by ^{1}H NMR). This decrease in the rate of the photoreaction of **2** is consistent with the increase in the distance between the two ethylenic bonds in the crystal structure of **2** (3.94 Å in **2** vs 3.65 and 3.73 Å in **3**) and might be assigned to a change in the intermolecular distance as the reaction proceeds.[19] The variation of the experimental parameters such as the wavelength and the reaction time did not induce any higher yield, but investigations aiming at the optimization of this reaction are far beyond the scope of this article. However, this partial [2 + 2] photocyclization reaction of unit **2** also confirmed the ability of 3-styrylthiophene to react under UV irradiation.

Synthesis of Block Oligomers. The crystal structures of olefins **2** and **3** have demonstrated that a $\pi-\pi$ interaction between the aromatic and thiophene rings is capable of self-assembling the compounds in columnar systems with great reliability and predictability. The columnar arrangement of compounds **2** and **3** and their systematic face-to-face organization raise another challenge. It could be assumed that identical supramolecular arrangements may occur at the macromolecular level for polythiophenes flanked by styryl substituents along the main chain. The interactions between individual $\pi-\pi$ stacked groups should cooperate and exert a high level of control over the supramolecular organization.

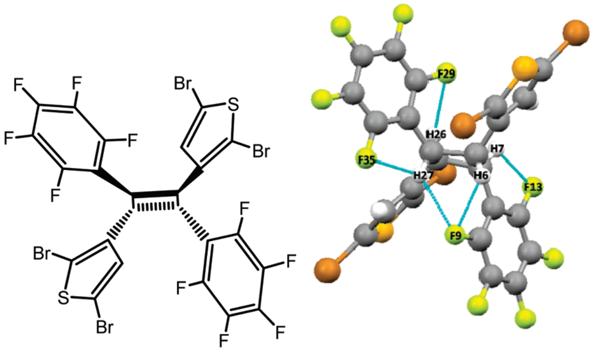

FIGURE 5. X-ray structure of cycloadduct **4** obtained by photocyclization of olefin **3**; the structure is locked by steric hindrance. Colors are as follows: gray, carbon; white, hydrogen; brown, bromine; yellow, fluorine; orange, sulfur atoms. Blue dotted lines represent short H···F contacts.

Recently, a similar approach has been developed to attach electroactive donor−acceptor polymeric blocks, using intermolecular $\pi-\pi$ interactions in a concerted manner.[21] On the basis of this concept, it was decided to exploit the styryl monomers **2** and **3** as building units for the formation of self-complementary supramolecular oligomers. We selected to synthesize low molecular weight block co-oligomers based on poly(3-styrylthiophene) (P3ST) or poly(3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene) (P3STF) linked to a poly(3-hexylthiophene) (P3HT) sequence in a 1:1 ratio of P3HT/P3ST and P3HT/P3STF. As previously stated, the incorporation of the P3HT segment was motivated by a combination of physical properties such as good solubility, chemical stability, and excellent electronic properties, which make P3HT one of the most attractive building blocks for elaborating conjugated block co-oligomers.[22] The preparation of poly(3-hexylthiophene)-*b*-poly(3-styrylthiophene) (P3HT-*b*-P3ST) **5** and poly(3-hexylthiophene)-*b*-poly(3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene) (P3HT-*b*-P3STF) **6** has been carried out by GRIM-type polymerization. This synthetic method represents an efficient strategy for the construction of regioregular polythiophenes combining soft and safe operating conditions.[9,10,23] Moreover the "living" chain growth mechanism of the GRIM reaction might afford straightforward access to regioregular block co-oligomers according to a one-pot procedure.[22c,24]

Prior to any copolymerization, some preliminary homopolymerization reactions of **2** and **3** have been attempted. Despite the efficiency of the GRIM process, the resulting poly(3-styrylthiophene) (P3ST) and poly(3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene) (P3STF) proved highly insoluble even for polymerization degrees (DP) lower than 20, making any spectroscopic and chromatographic analysis impossible. This insolubility led us to associate P3ST and

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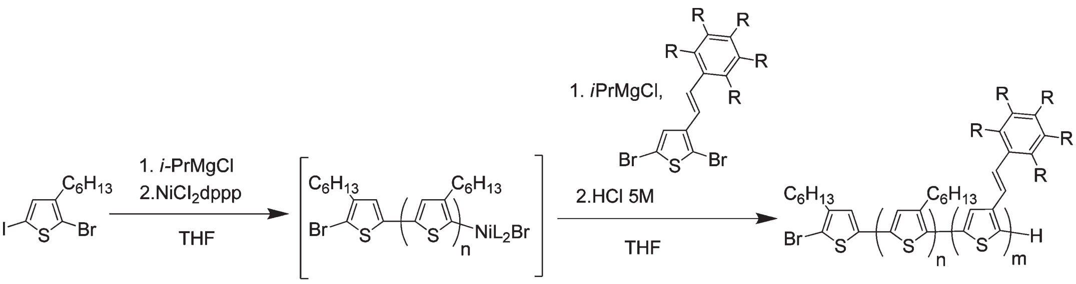
SCHEME 3. One-Pot Synthesis of Block Cooligomers 5 and 6



5 R = H
6 R = F

P3STF (of low molecular weight) into soluble poly(3-hexylthiophene) sequences. Block co-oligomers with low degrees of polymerization (DP ~20) were prepared. Such an oligomeric structure should be much easier to characterize than the polymeric substance and could be considered as a model for the polymer physical behavior, as well.

The synthetic route to P3HT-*b*-P3ST **5** and P3HT-*b*-P3STF **6** starts with the formation of a controlled P3HT fragment from 2-bromo-3-hexyl-5-iodothiophene (B3HT), as shown in Scheme 3. For this purpose, the GRIM polymerization of B3HT was performed with Ni(dppp)Cl_2 catalyst in THF for an initial monomer-to-initiator ratio of 10.[11] After 2 h at rt, a few drops of the crude mixture were withdrawn to confirm complete monomer conversion (DP ~9 as estimated by ^{1}H NMR). Subsequently, the preformed Grignard reagent of styrylthiophene **2** or 2′,3′,4′,5′,6′-pentafluorostyrylthiophene **3** were allowed to react for 2 h with the living P3HT oligomer chains, leading in a one-pot procedure to compounds **5** and **6** (after quick acidic termination reaction). As expected, the covalent association of low molecular weight P3ST or P3STF to a few units of 3HT allowed for recovery of soluble P3HT-*b*-P3ST and P3HT-*b*-P3STF co-oligomers.

The IR spectrum of **5** allowed to identify the characteristic ν_{C-H} absorption at 2925 cm^{-1} associated with the hexyl chain and the intense $\nu_{C=C}$ band at 3057 cm^{-1} assigned to the phenyl group. As far as the fluorinated compound **6** is concerned, the same ν_{C-H} band is observed at 2928 cm^{-1} and the ν_{C-F} band at 1493 cm^{-1} supports the presence of a fluorinated group in the molecular structure.

In both cases, the ^{1}H NMR spectra of **5** and **6** showed four signals in the range 0.8−2.9 ppm corresponding to the methylene and methyl protons of the 3-hexylthiophene units. The presence of the vinylic protons in the region between 6.5 and 7.4 ppm and the 4-proton on the aromatic thiophene ring at 6.98 ppm (a typical value for regioregular polythiophene) was confirmed for **5** and **6**.[9a] A broad signal was observed at 7.30 ppm, consistent with phenyl rings in compound **5**.

Integration parameters of appropriate signals (vinylic protons of styryl groups and methylene ones of hexyl chains) brought relevant information about the ratio of each block. Indeed, the P3HT/P3ST ratio in block co-oligomer **5** was around 56:44, and a nearly equimolar quantity (49:51) was observed for P3HT-*b*-P3STF **6**, which is very similar to the target amount (50/50) for each polymerization reaction. It is worth noting that ^{19}F NMR spectra of **6** exhibits three multiplets between −142 and −163 ppm, which is in good agreement with values previously found for **3**, proving the incorporation of the 3-2′,3′,4′,5′,6′-pentafluorostyryl fragment in **6**. Finally, both diblock topologies were assessed by GPC analyses by the appearance of monomodal traces (P3HT-b-P3ST **5**, M_n = 1800 g mol^{-1}, PDI = 1.58; and P3HT-b-P3STF **6**, M_n = 3200 g mol^{-1}, PDI = 1.38) recorded at lower elution volume with respect to the starting P3HT macroinitiatior.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry analyses of **5** and **6** confirmed both the covalent association of ST(F) and HT units by the combination of x units of 3-hexylthiophene with y units of 3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene or 3-styrylthiophene and exhibited a set of peaks corresponding to Br/H chain ends (see Figures S12 and S13 available in Supporting Information). Maximum molecular weights of about 3000−3100 g mol^{-1} (i.e, DP ~17−18) were observed in the MALDI-TOF spectra. Such values are in perfect agreement with that expected (DP ~20).

The UV−vis absorption spectra of P3HT-*b*-P3ST **5** and P3HT-*b*-P3STF **6** in $CHCl_3$ show two major bands at 305 nm and in the 400−450 nm spectral region (Figure S14 in Supporting Information). The high energy band at 305 nm is associated with the pendant styryl moieties, whereas the HOMO−LUMO transitions corresponding to the polythiophene backbones **5** and **6** appear at 425 and 440 nm, respectively.[25] In the solid state (Figure S15 in Supporting Information), the λ_{max} in the 400−450 nm of the two co-oligomers **5** and **6** are red-shifted respectively by about 40 nm, as compared to the values in solution. This band attributed to the $\pi-\pi^*$ interband transition of unsaturated bonds in polythiophenes is very sensitive to the effective conjugation length.[26] Indeed, the confinement of the polymer chains in the condensed phase is anticipated to support a planar arrangement of the adjacent thiophene rings and to enhance the delocalization of electrons within phenyl groups and the polythiophene backbone. However, this red shift obtained for co-oligomers **5** and **6** in the solid state is less significant than that previously obtained for P3HT (~100 nm), indicating a lower increase in the planarity of P3HT-*b*-P3ST and P3HT-*b*-P3STF chains when going to the solid state. The thermal properties of these polythiophene-based oligomers were also studied by TGA analysis (Figure S16 in Supporting Information). Both compounds **5** and **6** show an identical behavior characterized by a weight loss above 400 °C due to the decomposition of P3HT segments, as previously described

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in the literature.[27] A second weight loss is also observed from 250 to 400 °C for **6**, which may be assigned to the degradation of the 2′,3′,4′,5′,6′-pentafluorostyryl moieties. Finally, the DSC thermograms of polythiophenes **5** and **6** exhibit a melting point transition around 200 °C (Figure S17 in Supporting Information).

Photoirradiation of Oligothiophenes. Taking into account the ease of the [2 + 2]photocyclization reaction involving the compounds **2** and **3**, we suggested that the $\pi-\pi$ interactions would persist at the macromolecular level and self-assemble the co-oligomers **5** and **6** with the same accuracy. In a similar manner, the π-stacked aromatic groups should place the styryl double bonds according to Schmidt's rules (distance between the double bonds in the range 3.5−4.2 Å) and allow for a photoreaction in the solid state under UV irradiation. Consequently, we used an irradiation procedure that has mirrored the experimental proceedings applied for compounds **2** and **3**. Thus, the irradiation of finely powdered **5** and **6** was performed with a UV lamp at 340 nm for 18 h. Analysis of irradiated samples **5** and **6** has shown a sharp change in the composition upon irradiation, as evidenced by ^{1}H NMR spectroscopy. For both compounds, the ^{1}H NMR spectra show a new signal in the 5.15−5.30 ppm region assigned to a cyclobutane ring formation; a slight variation in the chemical shift values remains consistent with different structures and chemical environments as well. Thus, a limited amount of P3HT-*b*-P3ST **5** underwent a UV-induced [2 + 2] cycloaddition as highlighted by the new triplet recorded at 5.18 ppm (Figure S20 in Supporting Information). We assume that the strength of interaction involving the phenyl and thiophene rings is able to pack the oligomeric chains and consequently the double bonds at a distance spanning 3.5−4.2 Å. However, the conversion rate into cyclobutane units remains at a low level, closely related to the poor reactivity of 2,5-dibromo-3-styrylthiophene **2** under the same conditions.

Photoirradiation of the co-oligomer **6** has then been investigated. In this case, the UV light session of 18 h interestingly led to a significant response of cycloaddition reaction by ^{1}H NMR, namely, a clear peak at 5.30 ppm attributed to new cyclobutane protons (Figure S21 in Supporting Information). As seen for monomer **3** with respect to **2**, a higher conversion into the photoproduct is observed with co-oligomer **6**, which confirms a good superposition of pendant olefins with a small intermolecular distance. This results from stronger interactions between the thiophene and pentafluorobenzene rings packing the polythiophene backbones in the desirable arrangement. As far as the amount of cyclized styryl units is concerned, we can expect that only a limited number of double bonds is able to photoreact under UV irradiation. Indeed, the deformation of the polythiophene backbone due to the cyclobutane formation is expected to separate successive double bonds (distance >4.2 Å) and consequently prevent subsequent reactivity. Because of the relatively low solubility of photoirradiated cross-linked oligomers and the poor resolution of the ^{1}H NMR spectra, the double bond conversion into cyclobutane ring was roughly estimated to be in the range of 2−6% for compound **5** and 5−10% for **6**. Finally, the self-assembly of polythiophenes driven by $\pi-\pi$ interactions was clearly identified by a photochemical C−C bond formation of superimposed styryl groups for systems **5** and **6**.

Conclusion

In conclusion, we have demonstrated that the supramolecular organization of polythiophene chains can be controlled owing to the rational design of the constitutive units. The synthesis of new styryl and 2′,3′,4′,5′,6′-pentafluorostyryl-functionalized thiophene monomers and the characterization of their crystal structures are reported. The molecular arrangement of those molecules by $\pi-\pi$ aromatic interactions has allowed a [2 + 2] photocyclization reaction in the solid state, and the first X-ray structure of a 3-thiophene-substituted cyclobutane was obtained. The formation of regioregular block polythiophene co-oligomers with hexyl and styryl or 2′,3′,4′,5′,6′-pentafluorostyryl substituents was then performed and characterized by ^{1}H NMR, ^{19}F NMR, and MALDI-TOF mass spectroscopies. The incorporation of phenyl and 2′,3′,4′,5′,6′-pentafluorophenyl groups is expected to control the oligomeric chain orientation by $\pi-\pi$ interactions. Therefore, the evidence of precise nanostructured organizations was obtained by an original approach, namely the photoirradiation in the solid state of oligothiophene compounds. As a result, a UV-induced [2 + 2] cycloaddition reaction was clearly evidenced by the appearance of new signals assigned to cyclobutane protons, which confirmed the persistence of the $\pi-\pi$ interactions at the macromolecular level and the remarkable arrangement of the oligomeric chains relative to each other. This "bottom-up" construction of polythiophenes offers a reliable and highly efficient strategy for the elaboration of well-defined polymeric structures of higher molecular weight. The wide range of noncovalent interactions thereby suggests further promising results for the engineering of optoelectronic devices by recognition processes in a near future.

Experimental Section

2,5-Dibromo-3-styrylthiophene (2). Compound **2** was obtained according to a slightly modified literature procedure.[10] A 1.34 g (5 mmol) portion of **1** and benzyltriphenylphosphonium bromide (2.16 g, 5 mmol) were dispersed in THF (100 mL). To the resulting suspension was added DBU (1.53 mL, 10.23 mmol), and the resulting mixture was refluxed overnight under argon. The resulting reaction mixture was diluted with dichloromethane and washed with 1 mol L^{-1} hydrochloric acid. The organic layer was separated and dried over magnesium sulfate, and the solvents removed with a rotary evaporator. The residue was purified on silica using ethyl CH_2Cl_2/hexane (1:1) as eluent, affording **2** as a mixture of *E*/*Z* isomers in 78% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ: 7.70−7.22 (m, 11 H), 7.00 (d, 1 H, J_{trans} = 16.5 Hz), 6.89 (d, 1 H, J_{trans} = 16.5 Hz), 6.69 (d, 1 H, J_{cis} = 12.0 Hz), 6.60 (s, 1 H), 6.33 (d, 1 H, J_{cis} = 12.0 Hz).

Isomerization Procedure. Compound *E*/*Z* **2** (2 mmol) was dissolved in dichloromethane (50 mL), and iodine (1.52 g, 6 mmol) was added. The resulting mixture was stirred at room temperature for 7 days and then washed with a saturated solution of sodium thiosulfate and water. The organic layer was dried over magnesium sulfate and evaporated to dryness, and the residue was purified on silica using CH_2Cl_2/hexane (1:1) as eluent. Slow evaporation of a solution of **2** in CH_2Cl_2/hexane afforded white crystals in 92% yield. *E*-**2**: mp 58−60 °C. ^{1}H

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NMR (300 MHz, $CDCl_3$) δ: 7.70−7.22 (m, 5 H), 7.00 (d, 1 H, J_{trans} = 16.5 Hz), 6.89 (d, 1 H, J_{trans} = 16.5 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 139.1, 138.1, 131.3, 128.2, 127.8, 127.4, 120.0, 110.1. UV−vis (CH_2Cl_2): λ_{max} = 310 nm (ε = 42000). Anal. Calcd for $C_{12}H_8Br_2S$: C 41.89; H, 2.34; S, 9.32. Found: C 41.63; H 2.26, S 9.08

2,5-Dibromo-3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene (3). Under nitrogen, to a solution of 4-2′,3′,4′,5′,6′-pentafluorobenzyltriphenylphosphonium bromide (2.61 g, 5 mmol) in DMF (50 mL) was added slowly sodium hydride (0.24 g, 6 mmol, 60% dispersion in mineral oil). The reaction mixture was stirred during 45 min. Next, 1.34 g (5 mmol) of **1** was slowly added, and the mixture was heated at 60 °C overnight. Then, after addition of water (250 mL), a precipitate was obtained that was isolated by filtration. The residue was dissolved in CH_2Cl_2, dried under $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (9:1) as eluent. Slow evaporation of a solution of **3** in CH_2Cl_2 afforded white crystals. Yield: 1.69 g (78%); mp 103−105 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.32 (d, 1 H, $^3J_{H-H}$ = 16.5), 7.23 (s, 1 H), 6.77 (d, 1 H, $^3J_{H-H}$ = 16.5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 146.4, 143.1, 138.5, 128.1, 126.9, 126.8, 115.0, 113.0, 112.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −143.4 (2F), −157.4 (1F), −163.5 (2F). EI-MS (*m*/*z*): 434 (54, M^+), 355 (66, $M^+ - Br$), 336 (14, $M^+ - BrF$), 274 (100, $M^+ - 2\,Br$). UV−vis (CH_2Cl_2): λ_{max} = 308 nm (ε = 21600). Anal. Calcd for $C_{12}H_3Br_2F_5S$: C 33.21; H, 0.70; S, 7.39. Found: C 33.02; H 0.44, S 7.10

Photodimerization of Monomer 3. A 50 mg portion of finely powdered crystals of **3** was placed between two glass plates (76 × 26 mm) and was irradiated for 24 h. Compound **4** was isolated without further purification. Slow evaporation of **4** in $CHCl_3$ afforded yellowish crystals. Yield: 98%; mp 188−190 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.00 (s, 2 H), 4.81 (m, 4 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 146.9, 139.4, 135.8, 128.3, 112.2, 111.6, 110.2, 40.8, 38.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −140.9 (4F), −154.4 (2F), −161.8 (4F). Anal. Calcd for $C_{24}H_6Br_4F_1S_2$: C 33.21; H, 0.70; S, 7.39. Found: C 32.94; H 0.48, S 7.12

Typical Procedure for the Synthesis of Poly(3-hexylthiophene)-*b*-poly(3-styrylthiophene) (5) and Poly(3-hexylthiophene)-*b*-poly-(3-2′,3′,4′,5′,6′-pentafluorostyrylthiophene) (6). Two round-bottomed flasks (100 mL) equipped with three-way stopcocks were dried by heating under reduced pressure and cooled to room temperature. B3HT (1.12 g, 3 mmol) was dried by three successive azeotropic distillations with toluene, and then dry THF (15 mL) was added. A 2 mol/L solution of *i*-PrMgCl in THF (1.50 mL) was added via a syringe, and the mixture was stirred at 0 °C for 30 min (solution A). Solution A was added in one portion to the right amount of Ni(dppp)Cl_2 catalyst in THF (10 mL). In the other flask, 3 mmol of **2** (1.03 g) or **3** (1.30 g), previously dried by azeotropic distillation, was reacted with *i*-PrMgCl (1.50 mL) in the same manner (solution B). After stirring solution A for 3 h, solution B was added to the previous mixture via a syringe, and the resulting solution was stirred overnight. The reaction was quenched quickly by pouring HCl aq (5 M) into the solution and stirring for 0.5 h. Then, the mixture was precipitated in cold MeOH and filtered. The product was washed well with MeOH and hexane to afford a red solid. **5**: yield 0.66 g (63%). IR ($\tilde{\upsilon}_{C-H}$): 3057, 3025, 2953, 2925, 2854, 1494, 954 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.63−6.86 (m, 9H) 2.78 (m, 2 H), 1.68 (m, 2 H), 1.36 (m, 6 H), 0.88 (t, 3 H, $^3J_{H-H}$ = 6.0). UV−vis ($CHCl_3$): λ_{max} = 438 nm. **6**: yield 0.89 g (68%). IR ($\tilde{\upsilon}$C−H): 2928, 2857, 1512, 1493, 1004, 959 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (m, 1 H), 6.98 (s, br., 2 H), 6.83 (m, 1H), 2.80 (m, 2 H), 1.71 (m, 2 H), 1.35 (m, 6 H), 0.92 (m, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −143.1 (2F), −155.9 (1F), −163.0 (2F). UV−vis ($CHCl_3$): λ_{max} = 425 nm.

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Supporting Information Available: Materials and apparatus. Crystal and structure refinement data for compounds **2**−**4**. Thermal ellipsoid plot for compounds **2**−**4**. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (× 10^3) for **2**−**4**. Bond lengths (Å) and angles (deg) for for **2**−**4**. Anisotropic displacement paremeters (× 10^3) for **2**−**4**. ^1H NMR and $^{13}C\{^1H\}$ spectra of **2** in $CDCl_3$. Molecular packing diagram of **3** and **4**. ^{19}F and $^{13}C\{^1H\}$ NMR spectra of **3** and **4** in $CDCl_3$. MALDI-TOF spectra for P3HT-*b*-P3ST **5** and P3HT-*b*-P3STF **6**. UV−vis spectra of oligomers **5** and **6** in $CHCl_3$ and in solid state. TGA and DSC diagrams for P3HT-*b*-P3ST **5** and P3HT-b-P3STF **6**. ^1H NMR spectrum in $CDCl_3$ of co-oligomer **5** and after 3 days of co-oligomer **6** in the range of 4−8 ppm. ^1H NMR spectrum of co-oligomer **5** and 6 after 18 h of UV irradiation in the range of 4−8 ppm. This material is available free of charge via the Internet at http://pubs.acs.org.