Conjugated Polymers

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Picket-Fence Polythiophene and its Diblock Copolymers that Afford Microphase Separations Comprising a Stacked and an Isolated Polythiophene Ensemble**

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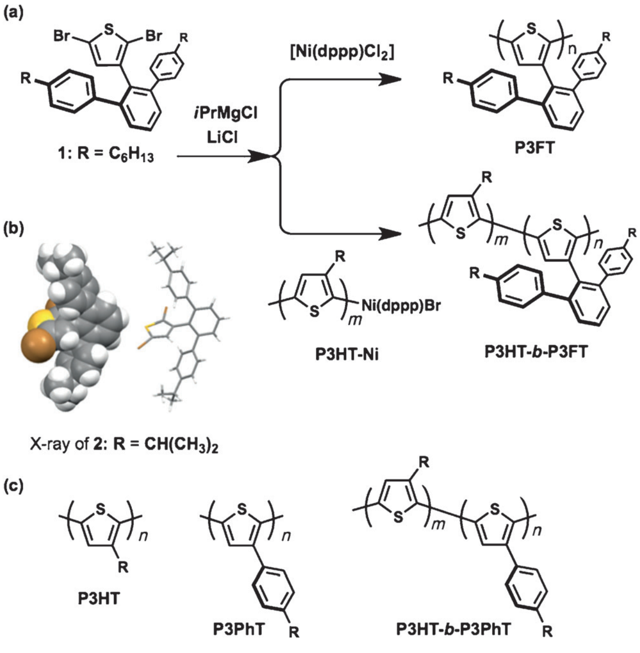
Abstract: *All-polythiophene diblock copolymers, comprising one unsheathed block and one fenced block, were synthesized through catalyst-transfer polycondensation. The unsheathed block self-assembles through π-π stacking, thereby inducing microphase separation. Consequently, we have succeeded in creating a microphase separation comprising an ensemble of stacked and isolated polythiophenes. This achievement could be extended to various unexplored applications as a result of the integration of the contrasting functions of the two blocks.*

The ability to control the supramolecular assembly of π-conjugated polymers (CPs) in thin films is essential for the development of organic optoelectronic devices because the collective functions and properties of CPs strongly depend on the interpolymer overlap of the molecular orbitals (i.e. π-π stacking).[1] Generating π-π stacks facilitates interwire charge-carrier transport,[2] whereas preventing π-π stacking leads to unique photophysical and mechanical properties.[3,4] The aim of our present study is to integrate both of these contrasting properties in a single polymeric film. Such a sophisticated design of CP-based materials should advance organic optoelectronics as complex materials lead to unprecedented functional systems.[5]

To this end, the approach based on the microphase separation (MPS) of block copolymers is straightforward and promising because it allows the assembly of more than two distinct properties in one system.[6] For example, MPSs comprising resist/sacrificial polymer domains and electron-/ion-transporting domains are useful for patterning technologies[6a] and electrochemical devices,[6b] respectively. CP-based MPSs have also attracted increasing attention as a result of the recent developments in catalyst-transfer polycondensation (CTP).[7,8] The CTP method has evolved so that even all-conjugated block copolymers can be obtained,[9,10] thereby leading to previously inaccessible MPSs such as those comprising crystalline/amorphous CP domains[9a] and p-type/n-type CP domains.[10] Likewise, our target—MPSs comprising stacked/isolated CP domains—can be realized through CTP; however, to the best of our knowledge, there has been no such report to date. It should be noted that, as recently reviewed by Bryan and McNeil,[7c] there are only a few monomers that can be efficiently polymerized by CTP and the method is as yet unestablished. As such, our additional interest in this study stems from whether isolated CPs, which have unique three-dimensional structures,[3,4] can be synthesized through quasi-living CTP. The main concern, in this context, is the proposed mechanism for CTP, which involves the formation of a Ni complex (Ni-π complex[7a] or associated pair[7b]) at the propagating terminus. Accordingly, CTP is assumed to be unfavorable for processing sterically hindered monomers, which we have designed will act as the isolated block. Remarkably though, our initial attempt demonstrated that the CTP method has unexplored potential, even for the synthesis of CPs with such distinctive three-dimensional structures. Herein, we report the synthesis through CTP of a new isolated CP, which we call picket-fence polythiophene[11] [poly(3-“fenced”-thiophene) (P3FT)], and its block copolymerization with poly(3-hexylthiophene) (P3HT) to create MPSs comprising an ensemble of stacked P3HT and isolated P3FT blocks.

2,5-Dibromo-3-“fenced”-thiophene monomers **1** and **2** (Scheme 1) were readily synthesized through well-established reactions and characterized by routine methods (see the Supporting Information). The X-ray crystal structure of **2** revealed steric protection of the thiophene monomer by the terphenyl “picket” fence. For CTP, **1** was first treated with isopropylmagnesium chloride in the presence of LiCl. The



Scheme 1. a) Synthesis of P3FT and its diblock copolymer, P3HT-*b*-P3FT. b) Monomer **2** in the crystallized form. c) Reference polymers that were synthesized and compared with P3FT. R = hexyl in the polymers. dppp = (1,3-bis(diphenylphosphino)propane.

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selectivity of the transmetalation for the bromide at the desired 5-position in preference to the one at the inverted 2-position was 81:19 (see Figure S1 in the Supporting Information). Subsequent addition of [Ni(dppp)Cl_2] to the reaction mixture initiated the polymerization, as briefly confirmed by a change in the color of the solution from pale yellow to red. It should be noted that the polymerization required a slightly elevated temperature (65 °C) because of the steric hindrance. A red powder was obtained after work-up of the reaction mixture by a common procedure.[12] The resulting polymer was highly soluble in common organic solvents and had a moderate molecular weight ($M_n = 15.3$ K, versus a polystyrene standard, which corresponds to about 32 repeating units). The ^{1}H NMR spectrum of the obtained P3FT confirmed a regioregular head-to-tail structure, which suggests that the "inverted" monomer was not involved in the polymerization (Figure 1 and see Figure S2 in the Supporting Information).

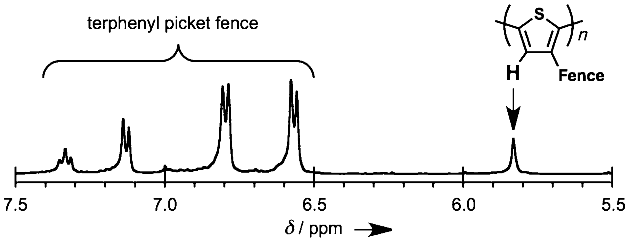

Figure 1. Aromatic region of the ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of P3FT: $M_n = 15.3$ K; PDI = 1.15; n = ca. 32, versus a polystyrene standard.

Importantly, the polydispersity index (PDI) of the P3FT was lower than 1.2 (see Figures S3 and S4 in the Supporting Information). All these results indicate that P3FT was synthesized in a chain-growth manner.[7–9] It should be noted, however, that our previously reported polythiophene[4d] could not be synthesized by the same procedure, which may shed light on the scope of the monomers, in terms of steric hindrance, for CTP (see Figure S5 in the Supporting Information). Although mechanistic details of the P3FT polymerization process are still unclear, we assume that after the reductive elimination step, the aromatic "fence" can act as a stepping stone and aid the transfer of the Ni catalyst to the propagating terminus. In fact, phenyl monomers are also known to have π-binding affinity for Ni^0, and are applicable to CTP.[13] In addition, such an acrobatic catalyst-transfer process has recently been suggested; in this case the Ni catalyst jumps across neighboring thiophene monomers that are linked through a nonconjugated spacer.[14]

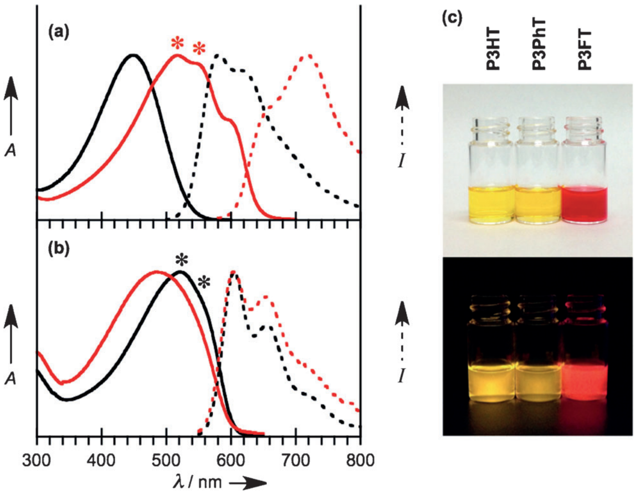

Figure 2. Normalized absorption (solid lines) and fluorescence (dotted lines) spectra of a) P3HT and b) P3FT in chloroform solution (black lines) and film form (red lines); electronic transitions marked as * can be attributed to planar polythiophene. c) Photographs of the solutions of P3HT, P3PhT, and P3FT under ambient (upper panel) and UV (lower panel) light.

Figure 2 compares the absorption and fluorescence spectra of solutions and films of P3HT and P3FT. As is well known, the absorption and fluorescence spectra of P3HT show a significant red-shift upon film formation because of the strong interchain π-π stacking (λ_{abs}: 450→600 nm: 5560 cm^{-1}).[15] In stark contrast, the absorption and fluorescence spectra of P3FT in solution and in a film are very similar. A small blue-shift observed in the absorption maximum of the film form relative to in solution (λ_{abs}: 523→488 nm: −1370 cm^{-1}), which has often been observed for other isolated CPs,[3] is probably due to conformational changes. The fluorescence quantum yield of the P3FT film (7 %) was higher than that of P3HT (2 %), which suggests that exciton migration is suppressed in the P3FT film. Furthermore, differential scanning calorimetry (DSC) measurements showed that P3FT was rather amorphous in nature (see Figure S6 in the Supporting Information), and ultraviolet photoelectron spectroscopy (UPS) revealed that a P3FT film had a larger ionization potential (ca. 5.3 eV) than a P3HT film (ca. 5.0 eV; see Figure S7 in the Supporting Information). These results indicate that terphenyl picket fences prevent the polythiophene backbone from forming π-π stacks.

Another intriguing feature of P3FT was discovered when comparing the absorption spectra of P3HT, P3PhT, and P3FT in solution (Figure 2c; see also Figure S8 in the Supporting Information). P3FT had an absorption maximum at 523 nm together with a shoulder at 561 nm, which are greatly red-shifted relative to those of P3HT ($\lambda_{max} = 450$ nm) and P3PhT ($\lambda_{max} = 453$ nm). These red-shifted electronic transitions were also observed for P3HT films (see * in Figure 2a,b), which are attributable to the 0–0 and 0–1 transitions of the planar polythiophene.[15] In addition, P3FT showed a lower oxidation potential (0.1 V versus ferrocene/ferrocenium (Fc/Fc^+)) than P3HT (0.2 V) in solution (see Figure S9 in the Supporting Information). These results suggest that P3FT exhibits better conjugation than P3HT and P3PhT in solution. A computer-generated model of P3FT confirmed that the regioregular picket fences interlock in a herringbone fashion and make the interior polythiophene backbone more planar (Figure 3a–c).[16] Furthermore, DFT calculations on the oligomers revealed the well-developed molecular orbitals of P3FT, which contrasts those of twisted P3HT (Figure 3d,e).[17] In fact, the proposed structure was supported by the ^{1}H NMR spectra: the signal for the β-proton of P3FT (5.83 ppm,

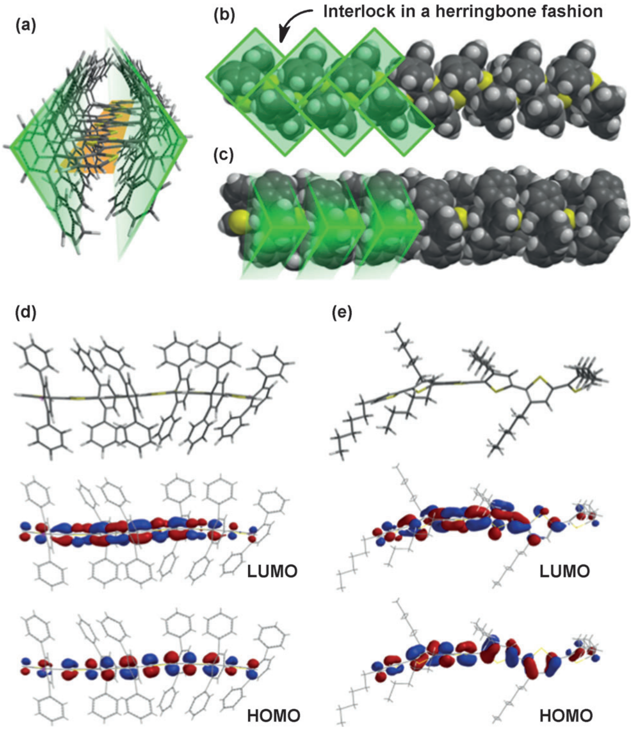

Figure 3. Computer-generated model of P3FT: a) axial, b) top, and c) lateral views. Note the interdigitation of the terphenyl picket fences in a herringbone fashion on both faces of the polythiophene backbone in (b), which extends the effective conjugation, as shown in (d). Structure and molecular orbitals of d) 3FT and e) 3HT hexamers (B3LYP/6-31G* levels).

Figure 1) appeared at a higher magnetic field than those of P3HT (6.98 ppm) and P3PhT (6.79 ppm), which can be attributed to the magnetic shielding by the aromatic picket fence (see Figure S10 in the Supporting Information). As such, P3FT is a unique polythiophene that features an isolated, planar backbone with a narrow polydispersity.

Encouraged by the above results, we performed block extension of P3FT from P3HT to synthesize poly(3-hexylthiophene)-*block*-poly(3-"fenced"-thiophene)s. As shown in Scheme 1, P3HT-Ni (PDI < 1.1) was first prepared according to the reported procedure,[9] and then used as a macroinitiator for the successive CTP of the P3FT block. After block copolymerization, the number average molecular weight (M_n) of the product as determined by gel permeation chromatography (GPC) increased relative to that of the macroinitiator P3HT, while maintaining the low PDI value (≤ 1.2; Figure 4a). This result illustrates the controlled propagation of the P3FT block from the P3HT block. We prepared several P3HT(x)-*b*-P3FT(y) species with different x/y ratios, which were determined on the basis of the ^{1}H NMR spectroscopic data (see Figure S11 in the Supporting Information; here, x and y represent the percentage composition of m and n, respectively). P3HT and P3FT have the same molar absorption coefficient at 476 nm ($\log\varepsilon_{476} = 3.88$), and so the spectra of these diblock polymers were normalized at this wavelength (Figure 4b). The spectra could be deconvoluted into those of P3HT and P3FT (see Figure S12 in the Supporting Information), and the determined ratios of the blocks was in good agreement with those determined by ^{1}H NMR spectroscopy. This result indicates that P3HT(x)-*b*-P3FT(y)s comprise two distinct polythiophenes (other basic photophysical properties of P3HT(x)-*b*-P3FT(y) can be found in Figure S13 and Tables S1 and S2 in the Supporting Information).

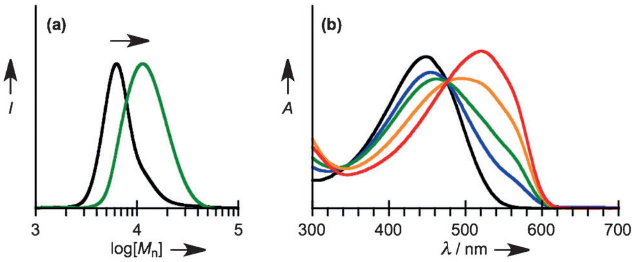

Figure 4. a) GPC retention curves of P3HT macroinitiator (black) and P3HT(55)-*b*-P3FT(45) (green). b) Absorption spectra of P3HT(x)-*b*-P3FT(y) for x/y ratios of 100:0 (black), 75:25 (blue), 55:45 (green), 25:75 (orange), and 0:100 (red) in chloroform, normalized at 476 nm.

The absorption spectra of P3HT-*b*-P3FT changed significantly upon spin-coating (Figure 5a and see Figure S14 in the Supporting Information). Given that the absorption spectrum of P3FT is insensitive to film formation (Figure 2b), the observed spectral change indicates the formation of π-π stacks by the P3HT block. The onset (650 nm) and shoulder (600 nm) of the absorption band of P3HT-*b*-P3FT indeed correspond with those of P3HT in its film form. Furthermore, wide-angle X-ray diffraction measurements showed characteristic peaks for a crystalline P3HT domain (see Figure S15 in the Supporting Information). It is noteworthy that these P3HT-*b*-P3FT films were still highly fluorescent relative to P3HT, P3PhT, and P3HT-*b*-P3PhT films (see Figure S16 in the Supporting Information). A spin-coated film of P3HT-*b*-P3FT on a silicon substrate was investigated by atomic force microscopy (AFM) after solvent annealing. Although P3HT(55)-*b*-P3FT(45) and P3HT(25)-*b*-P3FT(75) (with lower P3HT contents) did not show any particular morphol-

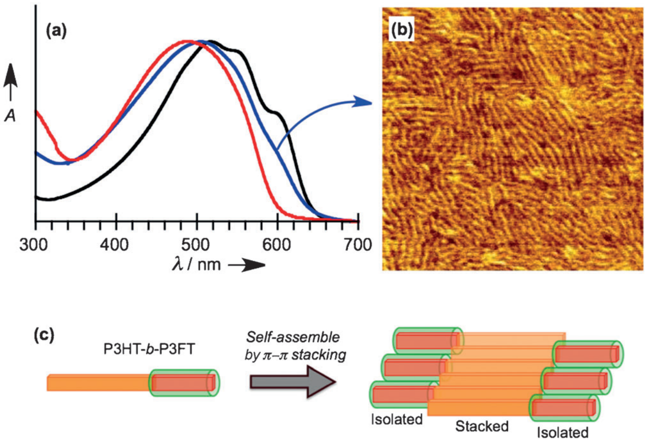

Figure 5. a) Normalized absorption spectra of P3HT (black), P3FT (red), and P3HT(75)-*b*-P3FT(25) (blue) in their film forms. b) AFM image of the microphase separation of P3HT(75)-*b*-P3FT(25) (700 nm × 700 nm; see Figure S18 in the Supporting Information for an image of a larger area). c) Illustration of the plausible self-assembled structure.

ogy (data not shown), P3HT(75)-*b*-P3FT(25) exhibited microphase separation, which resulted in a wormlike structure with a width of approximately 15 nm (Figure 5 b). Physical blending of P3HT and P3FT did not result in a well-defined morphology (see Figure S17 in the Supporting Information). We could thus conclude that the driving force for the microphase separation is the π-π stacking of the P3HT block. Considering the larger girth and shorter length of the P3FT block relative to the P3HT block, the periodicity must have emerged from an interdigitated structure (Figure 5 c). To the best of our knowledge, this is the first example of the microphase separation of all-conjugated diblock copolymers in which one block is stacked and the other is isolated.

Polythiophene films can be doped with iodine vapor. Interestingly, doped P3FT films are readily de-doped to their neutral undoped states within a few seconds once they are removed from the iodine vapor atmosphere (see Figure S19 in the Supporting Information). The doping/de-doping process of P3FT occurs quickly and reversibly, presumably because of the absence of the π-π stacking that stabilizes the charge carriers.[18] The changes in the absorption spectra of P3FT induced by doping/de-doping are accompanied by isosbestic points, whose presence can be attributed to a neutral/polaron equilibrium (see Figure S20 in the Supporting Information). As is well known, in contrast to P3FT, the doped state of P3HT is stable and electronically conductive (see Figure S21 in the Supporting Information). By taking advantage of the differences in the kinetic stability of the respective doped states of P3HT and P3FT, one can selectively dope the P3HT domain in a microphase separation. Consequently, the absorption spectrum of the iodine-doped P3HT-*b*-P3FT film consists of the summation of the spectra of doped P3HT and neutral P3FT (see Figure S22 in the Supporting Information). The conductivity of this film was $0.5\,\mathrm{S\,cm^{-1}}$, which is comparable to that of P3HT ($0.7\,\mathrm{S\,cm^{-1}}$) under the same conditions. Given that the P3FT domain in the doped P3HT-*b*-P3FT film is not electronically conductive, the approximate 28 % decrease in the conductivity of P3HT-*b*-P3FT relative to that of the P3HT film is reasonable. Hence, we assert that the stacked P3HT domain provides a continuous carrier transport pathway in the MPS of P3HT-*b*-P3FT films.[19]

In conclusion, the present study has revealed an unexplored potential of the CTP method in terms of steric hindrance, along with a demonstration of the chain-growth polymerization of isolated CPs. P3FT has a fenced and well-developed conjugated backbone with a narrow polydispersity (PDI ≤ 1.2), and therefore can be regarded as a new type of isolated CP.[3,4] Furthermore, on the basis of this finding, we have synthesized an all-polythiophene diblock copolymer, in which one block is unsheathed and the other is fenced. The unsheathed P3HT block self-assembles through π-π stacking, thereby inducing microphase separation. As a consequence, we have succeeded, for the first time, in creating a microphase separation comprising an ensemble of stacked and isolated polythiophenes. We believe that such sophisticated control over π-π stacking in a polymeric thin film will extend the use of these materials to various unprecedented applications as a result of the synergy of the contrasting properties of the two blocks.

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