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14. ABSTRACT A novel polythiophene -DBAB- type block copolymer system has been developed, where D is a new sulfide derivatized polythiophene donor block, A is a fluorine derivatized polythiophene acceptor block, and B is a non conjugated and flexible bridge chain. In donor block, a dithiathiothiophene ring derivatized polythiophene was used due to it is chemically more stable than the no-ring analogs. This structure also drastically limits the large steric hindrance in non-cyclized ones and is expected to result in high electrical conductivity. Additionally, the monomers have no possibility for α, β' or β, β' coupling during the polymerization. Sulfur is also known to be more electron donating and electro polarizable than oxygen. Most importantly, a fluorine derivatized polythiophene acceptor block has also been successfully developed. The fluorine substituted groups are known to be more easily phase separated from hydrocarbon groups due to their hydrophilicity differences, therefore, nano phase separation between the donor and acceptor blocks would be greatly enhanced. The newly developed polythiophenes have been characterized using spectroscopic, electrochemical, and electron microscopic methods.					
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FINAL PERFORMANCE REPORT

On

“Novel Nano-phase Ordered Polymer System for Efficient Photovoltaic Applications”

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1. PROJECT OBJECTIVE

The main objective of this project is to develop a novel nano phase ordered donor-bridge-acceptor (DBA or -DBAB-) type block copolymer systems for potential high efficient, lightweight, cost effective, and flexible shape thin film optoelectronic applications, including 'plastic' photovoltaic or photodiode device applications.

2. PROJECT EXECUTIVE AND STATUS OVERVIEW

During the three-year project period, a novel polythiophene -DBAB- type block copolymer system has been developed, where D is a new sulfide derivatized polythiophene donor block, A is a fluorine derivatized polythiophene acceptor block, and B is a non conjugated and flexible bridge chain (Fig. 1). In donor block, a dithiathophene ring derivatized polythiophene was used due to it is chemically more stable than the no-ring analogs. This structure also drastically limits the large steric hindrance in non-cyclized ones and is expected to result in high electrical conductivity. Additionally, the monomers have no possibility for α,β' or β,β' coupling during the polymerization. The ring structure also helps reducing the band gap of polymer compared to a similar length mono substituted polythiophene chain because the ring does not cause a detrimental steric twist of the polymer out of conjugation. Sulfur is also known to be more electron donating and electro polarizable than oxygen. Most importantly, a fluorine derivatized polythiophene acceptor block (shown in Fig. 2) has also been successfully developed. The fluorine substituted groups are known to be more easily phase separated from hydrocarbon groups due to their hydrophilicity differences, therefore, nano phase separation between the donor and acceptor blocks would be greatly enhanced. In comparison to poly-p-phenylenevinylene (PPV) -DBAB- type conjugated block polymers developed in our lab previously, polythiophenes are known to be chemically more robust, have lower energy gaps, and their stereo regio-regular analogs are known to have a tendency of self-assemble into more ordered supra-molecular morphological structures. Such morphological structures had been known to enhance charge mobility significantly. The newly developed polythiophenes have been characterized using spectroscopic, electrochemical, and electron microscopic methods. A 'plastic' solar cell based on polythiophene is expected to be more chemical stable and more efficient than the PPV analogs.

3. PROJECT KEY TECHNICAL ACCOMPLISHMENTS

Development of a Novel -DBAB- Type Polythiophene Block Copolymer

SYNOPSIS

Polythiophenes are a class of important conjugated polymers that have great potential for optoelectronic applications. Polythiophenes are known for their better chemical stability and easier self-assembly than poly-p-phenylenevinylenes or PPV

systems. In this report, the development of a new -BABD- type block copolymer containing poly(hexylene dithiathophene) PHDTT as a donor (D) block, a fluorinated ester polythiophene PTFS as an acceptor (A) block, and a four carbon aliphatic hydrocarbon chains as a bridge (B) is described. By using 3, 4-dialkylthiophene donor monomers, the large steric hindrance of copolymer is drastically limited. The monomers have no possibility for α,β' or β,β' coupling during the polymerization. The final -DBAB- block copolymer has a Mw of 18K Dalton and was soluble in CHCl_3 . In solution, it exhibited a band gap of 2.5 eV. Photoluminescent (PL) excitation and emission showed maxima at 360 nm and 585 nm respectively. The PL of a block copolymer thin film quenched over 95% compared to a simple donor/acceptor blend sample.

INTRODUCTION

Conjugated polymers are a new class of materials that combine the electronic and optical properties of inorganic semi-conductors with the processability of plastics. Recently, polymer solar cells have been developed based on the concept of donor and acceptor bulk heterojunction.¹⁻⁵ In an organic photovoltaic material, light induced excitons can typically diffuse 10-50 nm before decay, and the charged carriers (electron and holes) are generated mainly at the interface between the donors and acceptors where the electrons transferred to the acceptor phase, or the holes transferred to the donor phase. Then the carriers diffuse and are collected at the electrodes.⁵ Since the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the materials are critical for photon capture, carrier generation and recombination, suitable functional groups attached to the polymer main chain should be adjustable in order to fine-tune the HOMO and the LUMO levels.

Solution-processable conjugated polymers are likely to play an important role in low cost solar cell fabrications. However, since amorphous conjugated polymers have relatively low charge mobility compared to crystalline inorganic semiconductors, it is important to improve charge transport via molecular self-assembly and organized packing to achieve good performance of the cell. One way is to use block copolymers. Block copolymer phase separation and behavior has been known for decades.^{7,9,2} Donor/acceptor block copolymers offer some intrinsic advantages over donor/acceptor bilayer or blend for bulk heterojunction photovoltaic devices. For instance, when annealed above their melting or glass transition temperature, block copolymers may incur nano phase separation. The morphology of block copolymers is affected by a number of factors, including chemical structures, block size, substituted side chains, processing conditions, etc. When a donor conjugated polymer was connected directly to an acceptor conjugated block, energy transfer from higher band gap block to a lower gap one was observed, but no charge separation was detected.⁹⁻¹² This was possibly due to a fast electron-hole recombination via conjugated junction. To solve this problem, a PPV -DBAB- type block copolymer has been recently developed in our lab.^{7,19-26} When conjugated chains are self-assembled, π orbital can stack up in an orderly fashion. A bridge unit with high band gap would hinder the fast charge recombination, yet electron-hole separation can still proceed effectively through σ bonds or through space under photo excitations.¹³⁻¹⁴ The flexibility of the bridge units also enable easier phase separation of the rigid donor and acceptor conjugated blocks and causes less conjugation distortion.

The electronic and photonic properties of polyalkylthiophenes with side chains are remarkably sensitive to chemical and electrochemical perturbations, chemical structure, and morphology in solid states. These properties have made polythiophenes with variety side chains very interesting materials for optoelectronic applications.²³⁻³⁰ A synthetic strategy that would enable the functionalization of the thiophene after initial polymerization is very critical, as it allows for a simple generation of plethora of polythiophenes.⁵⁻¹⁰ We have selected dithiathophene derivatized polythiophene as donor block because disubstituted polythiophenes limit large steric hindrance shown for mono substituted polythiophene. To date, only a few studies of mercapto-substituted polythiophene have been reported. We chose fluorinated block polymer as an acceptor because of their excellent thermal stability, chemical and oxidative resistance. It has been shown that polythiophenes substituted with semifluorinated alkyl side chains have a great tendency of self-organization. Molecules consisting of fluorocarbon segments form lyotropic mesophases assemblies and smectic-like structures owing to micro or nano phase segregation arising from the immiscibility of their blocks. The nano phase segregation of perfluorinated alkyl chains also gives rise to layered structures in thin films of adsorbed polymers.^{19,45}

EXPERIMENTAL AND MATERIALS SYNTHESIS (See Appendix)

RESULTS AND DISCUSSION

The synthesized polythiophene -BABD- block copolymer was characterized by ¹H NMR, ¹³C NMR, GPC, UV-VIS, PL, DSC/TGA, CV and electron microscopy. The ¹H NMR aldehyde peaks for both donor and acceptor block appears at δ 10-10.5 (s) ppm, with ¹³C peak at 182 ppm as shown in Figure 2. NMR analysis shows all terminal aldehyde groups from the donor and acceptor disappeared after the block copolymer formed as shown in Figure 3. Acceptor block was orange-red color with very strong photoluminescence (PL) emission, while the donor block PL emission was relatively weak. This was possibly due to a PL quenching by the impurities in donor block samples, such as iron ion catalyst left in the polymer after synthesis. Further characterization is underway. The synthesized final -BABD- block copolymers were dark red-brownish color with a very weak luminescence.

Molecular Weight Analysis: Weight average molecular weight M_w and the polydispersity PD of all polymers were analyzed by GPC in THF. The repeat units of block copolymers were estimated from the M_w . From GPC analysis, the PHDTT donor block has a PD of 1.2, an M_w of about 3000g/mol corresponding to an average repeat units of 18, and an average size of 6 nm. The PTFS acceptor block has an M_w of about 15000g/mol corresponding to an average 54 repeat units and average size of 19 nm. The results of both block sizes were also confirmed from integration of hydrogen atoms in NMR spectra. The measured molecular weight of soluble part of final -BABD- block copolymer is about 18k, corresponding to the sum of roughly one acceptor block and one donor block. Since the final block copolymer was partially soluble in THF, and all polymer samples are filtered via a 0.2 μ m filter before GPC measurements, some higher molecular weight samples that

were not soluble in THF may be left out in the filter. For this reason, we use -BADD-symbol instead of DBA to represent our actual block copolymer sample.

Thermal Analysis: Thermal analysis of acceptor PTFS revealed a glass transition temperature (T_g) at 129°C . For PHDTT donor, the T_g is about 110°C . For PTFS acceptor block, the thermogravimetric analysis (TGA, under nitrogen gas atmosphere) showed a first weight drop starts at 83°C and the sample loses about 70% of its weight by 540°C . While the second major weight loss was believed to be due to decomposition, the cause of the first shallow weight loss was not clear. The donor block weight drop starts at 170°C and loses about 65% of its weight by 270°C . The weight drop in oxygen starts at $\sim 90^\circ\text{C}$ and 73°C for the donor and acceptor block respectively and results in 93% weight loss by 240°C and 493°C respectively for PHDTT and PTFS. By comparison, final block polymer exhibits much better thermal stability in nitrogen up to 220°C and about 175°C in oxygen before weight drop starts, higher than donor or acceptor blocks as shown in Figure 4. The DSC thermogram of final copolymer PT-FB under nitrogen atmosphere showed a broad T_g at 138°C . Upon the first heating and cooling cycle, the thermogram shows an irreversible exothermic peak at 288°C with the heating and cooling rate of $10^\circ\text{C}/\text{min}$. The exothermic peak is an irreversible event which could be due to energy released from new arrangement of π -stack of substituted functional groups on the thiophene.^{15,40-42} It is obvious that fluorine substitution indeed enhances the thermal stability dramatically.

UV-Vis Spectroscopy: For UV-Vis spectra in chloroform, the donor block has an absorption maximum at 360 nm, the acceptor absorption at 420 nm, the donor/acceptor blend exhibited an absorption maximum at 405 nm, and the final block exhibited an absorption maximum at 400 nm. The final block absorption was almost an overlay of the donor and acceptor blocks, and the blend sample spectrum appears to be just a simple overlap of the donor and acceptor spectrum with no obvious new absorptions (See Figure 5). There is no evidence of ground state electron transfer for either the block copolymer or the blend, i.e., the system indeed has a potential for photovoltaic applications.²⁰⁻³⁰ It is worth mentioning that the electronic properties of block copolymer PT-FB can be modulated by tuning the size or substitutions of either donor or acceptor block. The usual band for π - π^* polythiophene transition is at 450 nm which was used for comparison study. The small blue shift of final block suggest there is small steric hindrance produced by the formation of covalently bonded bulky system of donor and acceptor polymer which can be seen in solid state as well. This display is smaller than pure acceptor polymer but it is well above donor transition. All absorption spectra of chloroform solution have been normalized. They also display only one absorption band in the UV-Vis region similar to other polythiophene.^{22,23} The low energy peak onset appeared around 2.4 eV (516 nm) for PTFS acceptor block film, and 2.8 eV (442 nm) for PHDTT donor block film. The visible absorbance for donor polymer increases to the point that the solution becomes dark brownish when a solution exposes to air for long period of time. This was evidenced by the featureless absorption spectrum when completely oxidized. Some of sulfur substituted polythiophene compounds are found to be sensitive to air. It should be noted that these optical changes are similar to those observed for electrochemically deposited films. The polymer solution for solid film study should be cast and spray gently with air to yield homogeneous and pinhole free films on glass substrates. In solid state, the absorption

maximum of block copolymer appears at 382 nm, indicating a greater degree of planarity than in solution. The low energy peak of block copolymer of 2.5 eV (496 nm, onset of π - π^* transition) was confirmed by optical diffuse reflectance measurements and lies between that of PHDTT and PTFS. These energy band gaps were used to calculate the LUMO/HOMO levels of PT-FB.

Electrochemical Studies: The electrochemical properties of these polymers were studied using cyclic voltammetry (CV). A saturated silver electrode (SSE) was used as reference electrode, and scan rate was 100 mV/s. The electrolyte of 1.0 M tetrabutylammonium hexafluorophosphate (TBA-HFP) and Ferrocene (Fe/Fe^+ redox pair) was used as the internal standard for calibration purpose. The solution was typically degassed by dry nitrogen bubbling for 20 minutes prior to use and maintained under nitrogen blanket throughout each experiment. The electrochemical property of the polymer was studied in THF for donor block, acceptor block, and final block copolymer. The acceptor PTFS showed one oxidation process at +1.2 V/SSE and one cathodic process at -1.4 V/SSE (corresponding to an electronic band gap of 2.6 eV), whereas for PHDTT, an oxidation potential lower than acceptor block was seen +0.8 V and cathodic process at about -2.0 V (corresponding to an electronic band gap of about 2.8 eV). Combining spectroscopic and electrochemical data, the LUMO/HOMO levels of the PTFS acceptor block were about -3.0/-5.4 eV, whereas the LUMO/HOMO levels of the PHDTT donor block were -2.2/-5.0 eV. However, the block copolymer exhibited a high oxidation peak at +1.7 V and an reduction peak at -1.1 V as shown in Figure 6. The higher oxidation peak might be related to the formation of interchain π orbital stacking.⁴¹⁻⁴⁴ The anodic peak currents vary linearly with scan rates in range (-3.0)-(-2.0) V/s. This indicates the surface confined nature of the block polymer as has been reported in many polythiophene.²³ The film was brown-yellow in the neutral state and dark-brown in the oxidized state. The large potential hysteresis between oxidation and reduction of final block polymer is attributed to a number of factors such as diffusion of dopant ions in and out of the films, conformational relaxation of polymer chains between the rigid planar oxidized and flexible neutral states and film thickness.⁴³⁻⁴⁴

No significant electroactivity loss was seen after 80 cycles as the applied potential swept continuously between (0.0)-(2.1) V/s. For comparison, the electrochemical behavior of blend sample (50-50wt%) was also investigated with solution-cast films on a Pt electrode. It shows the anodic peak does not exist at +1.7 V, and the cathodic peak is a narrow peak at about -510 mV.

Photoluminescence Spectroscopy: The emission spectra of donor (D), acceptor (A), -DBAB- blocks and blend samples were measured for comparison. The spectra of photoluminescence (PL) excitation peaks of PTFS were observed in the violet region at 370 nm and 410 nm for the solution and thin film respectively. The solution emission peak was 555nm (yellow emission) and the thin film emission peak was 585 nm (yellow-orange) region. Both the excitation and emission spectra resulting from the thin film were red-shifted compare to those in solution, the same result was observed also for donor and final block copolymer. The spectra of (PL) excitation and emission of PHDTT donor were at 480 nm and 593 nm in solution and 510 nm and 609nm in solid state respectively. The final block copolymer red-shifted emission spectra is a bathochromic shift from 582 nm in

solution to 600 nm in solid film. The red shifts of emission are common in conjugated polymers and are generally attributed to a solid-state intermolecular π electron interactions and a backbone planarization. There is a small shoulder peak seen in thin film for excitation spectra of block copolymer in comparison to its emission peak as seen in Figure 7. A red shifted excitation spectra was also observed in solid state from 360 nm in solution to 392 nm in solid state.

In PL emission quenching studies, the content of polymer was prepared based on 10^{-2} M concentration of an original polymer solution and diluted 10^2 times each to see PL quenching effect. Samples were measured in room temperature in a four-sided quartz sample holder. The donor block has an emission maximum at 593 nm, the acceptor has an emission maximum at 555 nm, and the final block copolymer has a very weak emission at 585 nm. Both block copolymer and blend samples show the decrease of PL emission in lower concentration by diluting the samples. However, magnitudes of PL quenching become divergent as solution become more diluted (see Figure 8). The PL quenching of the final block was estimated at about 83% compared to that of the blend system shown in Figure 8. To measure the quenching for each solution, the maximum emission peak was used. This way we maximized the emission observed for each solution. The blend samples were made by 50-50wt% of acceptor and donor block. Bridge unit did not show any emission. The highest number of emission intensity was then normalized and plotted using blend samples versus block copolymers. The fact that block copolymer has a much quicker and deeper PL quenching slope compared to the blend indicated that photo induced electron transfer from the donor to acceptor via bridge indeed occurred.

Similar set of procedure was used for thin film measurements. PL quenching in solid state appeared much severe than in solution for both blend and block copolymer. This might be explained by the fact that the photo induced electron transfer in dilute solutions is mainly an intramolecular process, where in the blends, the quenching were due to both intermolecular collision and intramolecular charge separation. This is because in thin film, the donor and acceptor molecules are closer in space and can interact much better. The photo induced electron transfer process is therefore more efficient. The photoluminescence emission spectra of the final polythiophene -DBAB- film on glass substrate and blend samples were compared. From PL intensity-density analysis, we could estimate that the PL in final block film on glass was quenched by over 95% as compared to blend films. In blend samples of D/A, PL quenching was weak and it was also very sensitive to preparation of thin films or original solutions. This might be explained that the donor/acceptor interface in the -DBAB- block copolymer is much bigger and more uniform than the donor/acceptor blends. The data demonstrated that -DBAB- type block copolymer is indeed superior in comparison to blend systems on exciton quenching and therefore, favorable for photovoltaic functions. For UV-VIS absorption spectra, the results show no major new absorption bands in the final -DBAB- block copolymer spectra. This was an indication of no ground state electron transfer (chemical doping) occurred in final block. There is however, a broadening peak of excitation for final block as comparison to blend sample due to solid intermolecular interaction of block copolymer. To get consistence result, great care must be applied when solutions are made or spin coating of thin films are in progress. PL emission dynamic studies are also under way using argon ion

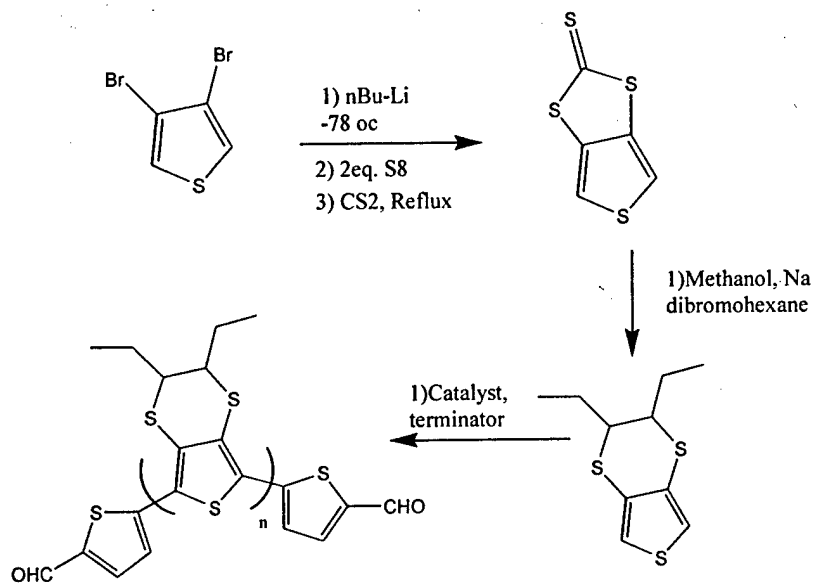
pumped with Ti-Sapphire laser system to confirm decaying of final block compared to blend samples.

Electron Microscopic Studies: Scanning electron microscopy (SEM) studies on cross sections of the polymer samples with 100 μm thickness showed irregular pattern phase separation for PHDTT/PTSF blend samples. The aggregation effect of blend polymer samples can possibly be due to the assembly of the side chains of fluorinated polymers which tends to be planar conjugated chains and will be self-organized into lamellae or micelle in solid state.⁴⁴ It has been known that fluorinated polymer can exhibit unusual properties because of hydrophobicity, rigidity and self-organization of perfluoroalkyl chains. The macro phase segregation observed in SEM picture is possibly due to the immiscibility of fluorocarbons and hydrocarbons.^{19,44} However, final block copolymer of -DBAB- film exhibited some morphological pattern with no obvious irregular macro phase separation as shown in Figure 9. Some macro phase pattern were observed when final block thin film formed on a silicon substrate. Previously, we have observed morphological phase separation of block copolymers were sensitive to block sizes and chemical compositions of polymers, and phase pattern might change as drying conditions of film changes. It was also found that the charge mobility could be influenced dramatically by the morphology of the films.³²⁻³⁷

CONCLUSION

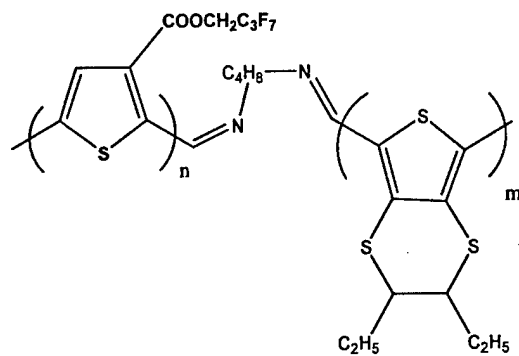
A novel -DBAB- type polythiophene block copolymer has been designed, synthesized, and characterized, and the morphology appears much better in the block copolymer than in the donor/acceptor blend at micron domain. This is possibly due to block copolymer intrinsic nano phase separation properties and fluorocarbon-hydrocarbon differences. The block copolymer is consisted of a PHDTT mercapto-substituted polythiophene donor block and a PTFS derivatized fluorinated acceptor block linked by a non conjugated and flexible bridge chain. Spectroscopic studies revealed that PL of the block copolymer quenched by nearly 95% relative to blend polymers in thin film. A comparison between blend and block copolymers shows a better thin film morphology in -DBAB- block copolymers. One advantage of this system is that functionalized block copolymers can be used to form a tailored nano-structured regioregular polythiophene copolymers with different functional groups. This -DBAB- block copolymer system therefore appears very attractive for developing light harvesting devices such as plastic photovoltaic cells. By forming ordered and nano phase separated block copolymer thin film, photo induced charge generation and transportation would be greatly optimized.

4. PROJECT RELATED FIGURES



Scheme 1.

-(B-A-B-D)- block co-polymer



Scheme 2.

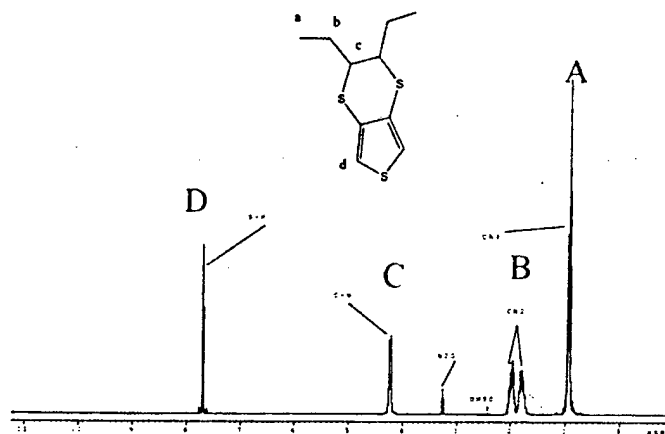


Figure 1. ¹H NMR Spectra of 3,4-Hexylene-dithiathophene.

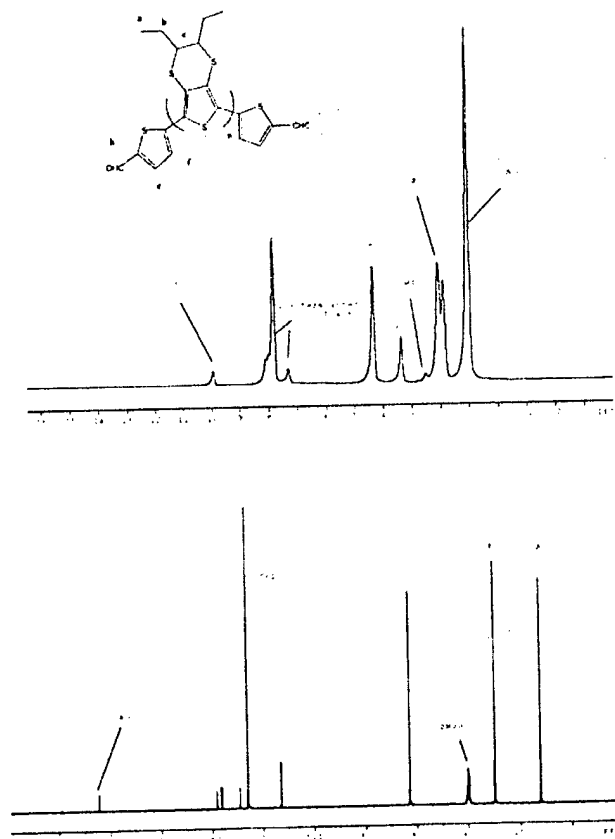


Figure 2. Top; ¹H NMR Spectra of Poly(3,4-hexylenedithiathophene), PHDTT; Bottom ¹³C NMR Spectra of PHDTT.

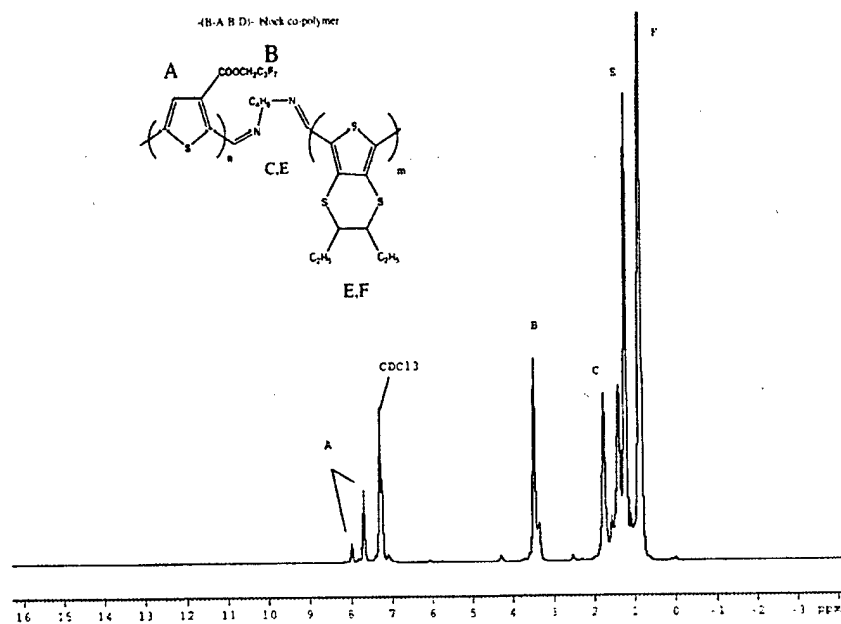


Figure 3. ¹H NMR spectra of final polythiophene block copolymer PT-FB.

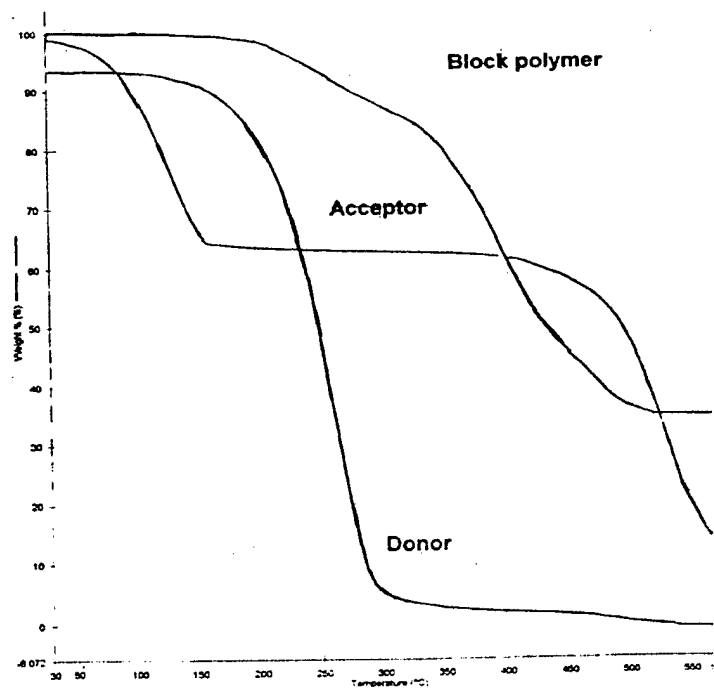


Figure 4. TGA thermograms of PHDTT, PTFS and final block copolymer PT-FB under nitrogen gas.

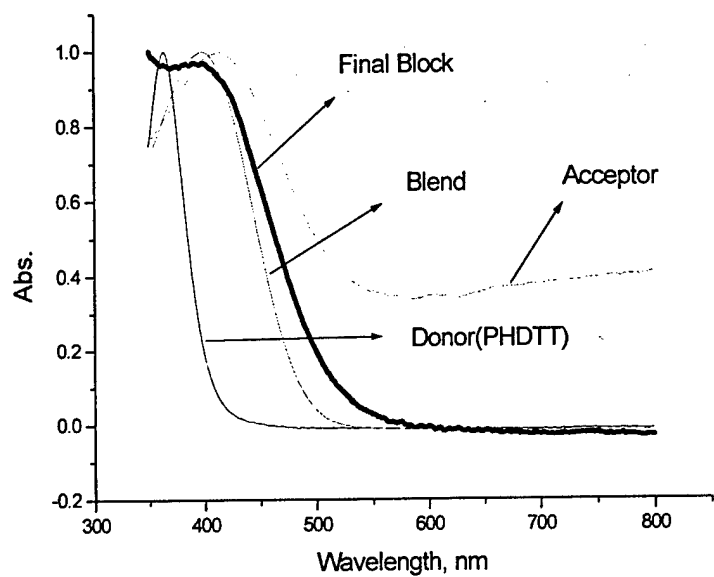


Figure 5. UV-VIS spectrum comparison between block donor, acceptor, blend and final block in chloroform.

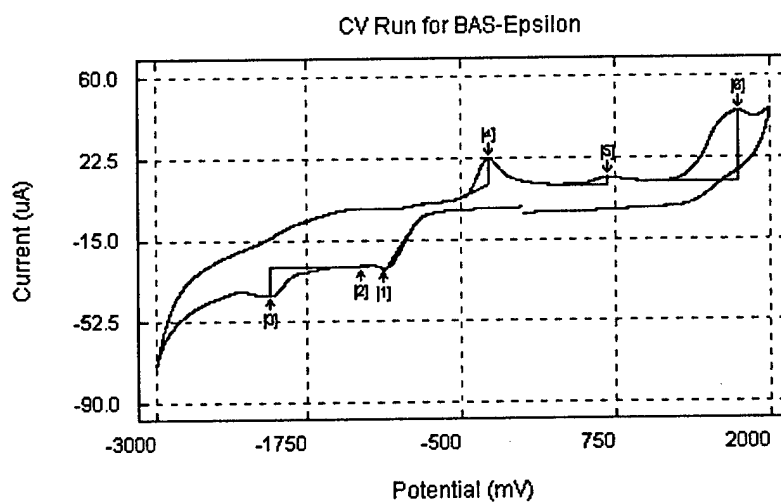


Figure 6. Typical cyclic voltammogram of final block film on a platinum electrode with sweep rate 100 mV s^{-1} .

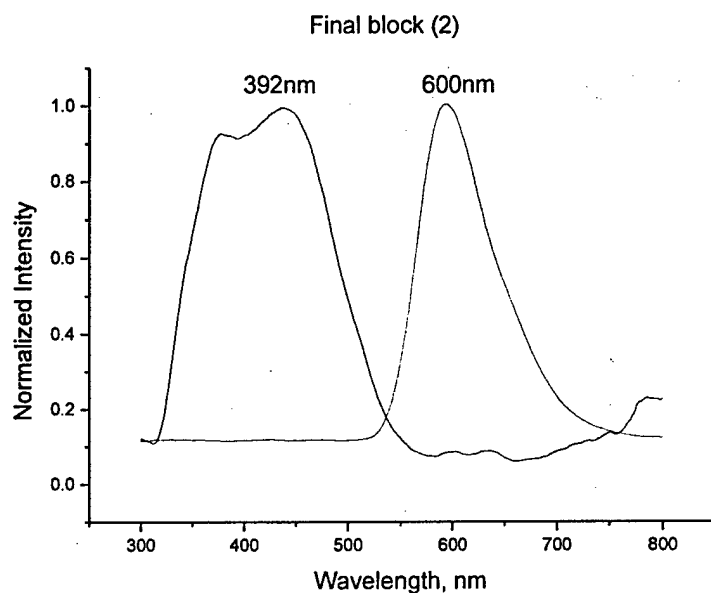


Figure 7. Thin film emission and excitation spectrum of final block. (Note: All peaks have been normalized).

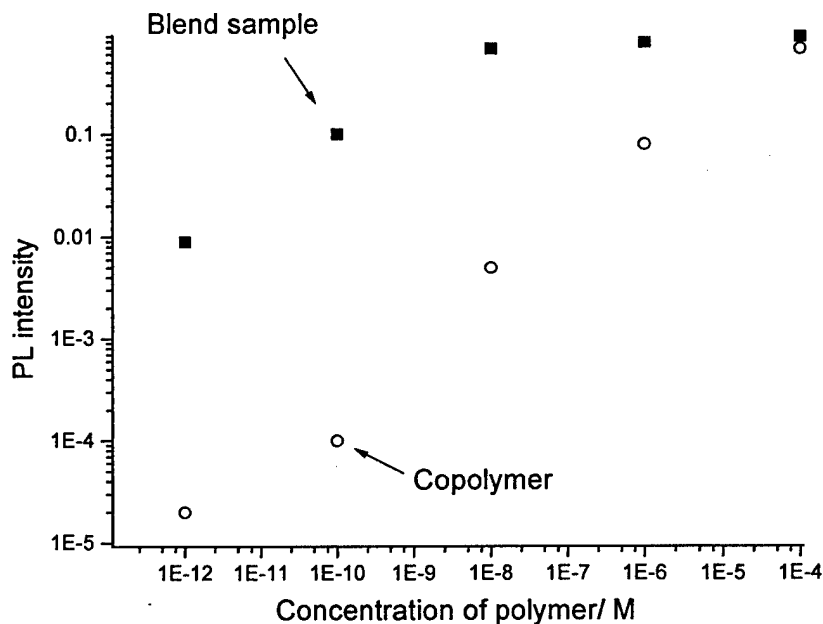


Figure 8. Comparison between the PL intensity of copolymers and blend samples in chloroform (PL intensity is normalized).

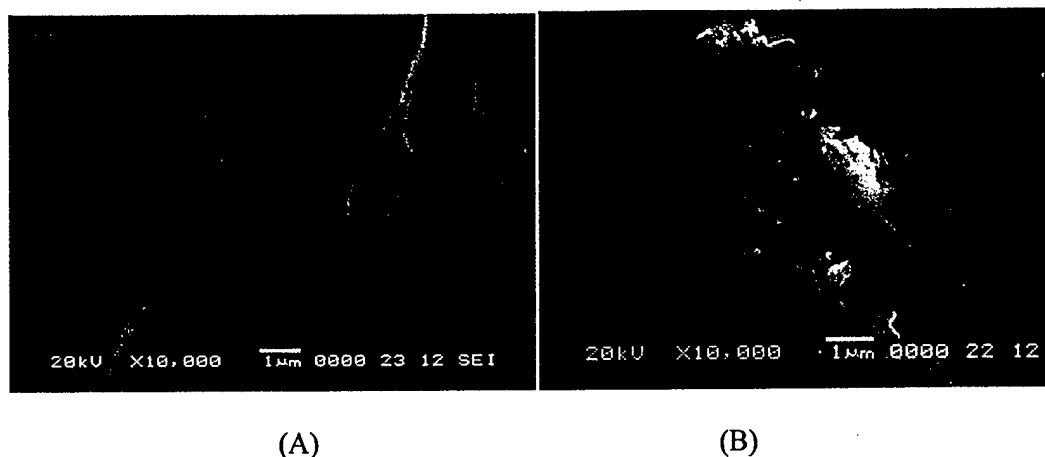


Figure 9. Comparison between cross section of copolymer (a) and blend sample (b) in solid state.

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6. PROJECT SUPPORTED PERSONNELS

The project PI, Professor Sam Sun, and two senior research faculty members (Drs. S. Maaref and S. Choi) who participated have been partially supported during the project

period. Though not budgeted, at least one graduate student (Miss Shanneth Thomas) and a number of undergraduate students participated and contributed significantly to this project, and they were supported by other federal grants and/or private foundations, e.g., from the Department of Education (Title III grant), the NSF (CREST grant), NASA (University Research Center grant), and the Dozoretz Foundation (undergraduate students).

7. PROJECT RELATED PUBLICATIONS

1. Sun, S. and Sariciftci, S., eds., *Organic Photovoltaics: Mechanisms, Materials and Devices*, CRC Press, Boca Raton, Florida, 2005 (ISBN 0-82475-963-X).
2. Sun, S. and Bonner, C., "Chapter 8: Optimizations of Organic Solar Cells in Both Space and Energy/Time Domains", in *Organic Photovoltaics: Mechanisms, Materials and Devices*, edited by Sun and Sariciftci, CRC Press, Boca Raton, Florida, 2005, pp 183-214.
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8. PROJECT RELATED PRESENTATIONS/LECTURES

1. Sun, S., "Optimizations of Organic Solar Cells", presentation at the 228th ACS National Meeting, Philadelphia, PA, August, **2004**.
2. Sun, S., *et al.*, "Conjugated Block Copolymers for Photovoltaics: Optimization of Photoelectric Efficiency in Both Space and Energy/Time Domains", presentation at the 2nd IECEC International Conference, Providence, RI, August, **2004**.
3. Sun, S., "Polymer morphology and energy levels versus photoelectric power conversion efficiencies: a preliminary account", presentation at SPIE 49th Annual meeting, Denver, Colorado, August, **2004**.
4. Sun, S.; *et al.*, "Center for Research and Education in Advanced Materials", presentation at NASA HBCU/MI 2004 Conference, Cleveland, OH, July, **2004**.
5. Sun, S. and Bonner, C., "Optimizing organic solar cells in both space and energy domains", presentation at ICSM-2004 Conference, Wollongong, Australia, June, **2004**.
6. Sun, S.; "Optimization of Organic Solar Cells", presentation at SCELL-2004, Badjoz, Spain, May, **2004**.
7. Sun, S., *et al.*, "Block Copolymers for Photovoltaics", presentation at SPIE Photonic-Europe Conference, Strausburg, France, April, **2004**.
8. Sun, S., "Improving Opto-electronic Efficiency via Bridged Donor and Acceptor Block Copolymers", presentation at the 227th ACS National Meeting, Anaheim, CA, March, **2004**.
9. Sun, S. "Block Copolymers for Photovoltaics: Toward Plastic Solar Cells", an invited seminar presentation at California State University, Northridge, California, March 29, **2004**.
10. Sun, S. "Block Copolymers for Photovoltaics: Toward Plastic Solar Cells", an invited seminar presentation at Vanderbilt University, Nashville, Tennessee, February 25, **2004**.
11. Sun, S.; Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S.; Ledbetter, A.; Bonner, C., "Block Copolymers for Optoelectronics", presentation at SPIE-APOC-2003 Conference, Wuhan, China, November, **2003**.
12. Sun, S.; "Design and Development of Conjugated Block Copolymers for Use in Photovoltaic Devices", presentation at SPIE 2003 Annual Convention, San Diego, California, August, **2003**.

13. Sun, S. "Toward Plastic Solar Cells", an invited seminar presentation in the Chemistry Department at University of Southern California (USC), Los Angeles, USA, August 1, 2003.

9. PROJECT GENERATED OR RELATED STUDENT THESIS

1. Z. Fan, "Synthesis and Characterization of A Novel Block Copolymer System Containing RO-PPV And SF-PPV-I Conjugated Blocks", MS Thesis, Norfolk State University, Norfolk, Virginia, July 2002.
2. S. Thomas, "Synthesis and Characterization of a new Acceptor (N-Type) Fluorinated and Terminal-Functionalized Polythiophene", MS Thesis, Norfolk State University, Norfolk, Virginia, August 2004.

10. HONORS/AWARDS

During the project period (2001-2004), the PI (Professor Sun) received several awards and honors at Norfolk State University. These include "Outstanding Mentoring" and "Outstanding Grantsmanship", "Outstanding Scholarly Activities", etc., which were awarded at NSU's School of Science and Technology Annual Awards Lunch/Banquet. Professor Sun was also invited to review technical publication papers or grant proposals on behalf of a number of scientific societies/publishers (ACS, SPIE, Elsevier), or funding agencies (NSF, Canadian Council of Arts) on the subject matter.

APPENDIX: MATERIALS SYNTHESIS DETAILS

Materials and Measurements

All starting materials, reagents and solvents were purchased from either Aldrich or Fisher unless noted otherwise. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. All solvents were distilled over sodium and benzophenone and then blown with dry inert gas. Polymer thin films were typically spin coated onto either regular glass micro-slides or onto one-side coated ITO conducting glass slides.

^1H NMR and proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz Spectrometer. TMS was used as internal reference standard. For monomer ^1H NMR spectra, 16 scans were usually taken. For ^{13}C NMR spectra, 2048 scans were typically taken to achieve a useful signal-to-noise ratio. For polymers, ^{13}C NMR spectra, 25000-50000 scans were typically taken. The FTIR spectra ($4000\text{-}550\text{ cm}^{-1}$) were obtained on a Nicolet Avator FTIR spectrometer. Typical 16 scans were collected for each sample. Homogeneous polymer thin films were formed on the KBr IR cell from drops of a diluted solution of linear polymer or an aliquot of polymer sample applied on the cell directly and followed by evaporation of solvent. Solid IR samples were made using KBr pellet technique.

Polymer molecular weights were measured employing a Viscotek TriSec T60/LR40 GPC (gel permeation chromatography) system with mobile phase of THF in ambient temperature. Polystyrene standards were used as the reference. Perkin-Elmer DSC-6 (differential scanning calorimeter) and TGA-6 (thermal gravimetric analysis) systems were employed to characterize the thermal stability of the polymer samples. The heating rate of $10^\circ\text{C}/\text{min}$ was used to obtain higher sensitivity and collect more data in each scan. A Varian Cary 5G UV-Vis-NIR double beam spectrophotometer was used to measure the absorbance of polymer solutions and film samples between 250-850 nm at room temperature. ISA Fluoromax-3 fluorescent spectrometer was used to measure photoluminescence. For thin film study, the bare ITO substrate is used as a reference. Photoluminescence (PL) was measured using an ISA Fluoromax-3 unit. The samples were measured between 200-850 nm at room temperature. Epsilon-100W electrochemical work station with analog filtering and RS-232 connection was used for Cyclic Voltammetry (CV) measurements.

Donor Block PHDTT

The synthetic scheme of disubstituted polythiophene is shown in Scheme 1.

Thieno[3,4-d]-1,3-dithiole-2-thione (1): A solution of 3,4 -dibromothiophene (4.95 g, 20.5 mmol) in anhydrous diethylether (30ml) was cooled to -78°C (dry ice and acetone) under nitrogen gas. To this stirred and pre-cooled solution, n-butyl-lithium (12.8 ml, 20.5 mmol, 1.6 M in hexane) was added via syringe. The solution was stirred for 0.5 h, and then sulfur (0.66, 20.6 mmol) was added and stirred for one hour. Second portion of n-butyllithium

and sulfur were added the same way as mentioned above and the mixture was allowed to come to room temperature. The solvent was removed under vacuum to get a yellow solid. To the yellow solid, 2N sodium hydroxide solution (50 ml) and carbon disulfide (20 ml) were added. The mixture was refluxed under nitrogen for six hours and then allowed to stand at room temperature overnight. The excess carbon disulfide was removed under vacuum, and the dark reaction mixture was filtered and washed with 2 × 30 ml of water to give a yellow solid. Recrystallization of solid from dichloromethane-hexane (5:1 (v/v)) gave 1.06 g (28% yield) of thieno[3,4-d]-1,3-dithiole-2-thione as amber needle^{43,44}. (Caution: if materials is exposed to air for long time, product will turn to a dark color). mp 142°C; ¹H NMR (DMSO) δ 7.1 (s, 2H); ¹³C NMR (DMSO) (¹H decoupled): δ 207.1, 127, 125; UV-VIS (CH₂Cl₂) λ_{max} 298 nm, IR (neat) 3038, 2916, 2895, 1481, 1409, 1329, 1375, 861, 779 cm⁻¹. Anal. Calcd for C₅H₂S₄: C, 31.57; H, 1.05; S, 67.36. Found: C, 31.32; H, 1.08; S, 67.29

3, 4-Hexylene-dithiathiophene (2): Sodium metal (0.167 g, 7.28 mmol) was added in one portion into a stirred and freshly distilled methanol (75 ml) under nitrogen. After the sodium dissolved completely, thieno[3,4-d]-1,3-dithiole-2-thione (0.570 g, 3.0 mmol) was added to the solution. The reaction mixture was left to react for one to two hours at 50°C under nitrogen. The product was a yellowish solution. To this solution 3,4 dibromohexane (0.939 g, 3.85 mmol) was added via syringe. After 24 hours at room temperature, the methanol was removed under vacuum and anhydrous ether (40 ml) was added. A yellow solid of 3,4-hexylenedithiathiophene was obtained when the ether was removed and product was chromatographed on a silica gel column with hexane as eluent, yield 78% (0.538g). NMR spectrum is shown in Figure 1. ¹H NMR (DMSO) δ 7.7 (sharp, s, 2H), 4.2 (m, J=1 Hz, 2H), 1.8, 2.0 (m, J=1 Hz, 4H), 0.9 (m, J=1 Hz, 6H); ¹³C NMR (DMSO) (¹H decoupled) δ 134.1, 120.7, 53.3, 25.9, 10.7; UV-VIS(CH₂Cl₂) λ_{max} 310 nm, IR (neat) 3049, 2816, 2795, 1433, 1424, 1375, 861, 778 cm⁻¹. Anal. Calcd for C₁₀H₁₄S₃: C, 52.17; H, 6.08; S, 41.74 Found: C, 52.20; H, 6.11; S, 41.52

Poly(3,4-hexylenedithiathiophene), Poly(HDTT) (3): Anhydrous FeCl₃ (0.85g, 5.2 mmol) was dissolved in 30 ml of dry CH₃CN and stirred for 20 min. To this red-orange solution, (0.296 g, 1.3 mmol) 3,4-hexylene-dithiathiophene (HDTT) in 20 ml of dry CH₃CN was added dropwise. A dark blue-green viscose liquid was formed immediately and the reaction mixture stirred for 30 minutes under nitrogen at room temperature. To quench the reaction, 2-thiophenecarboxaldehyde monomer (1.707g, 15.2 mmol) was added to the mixture. The reaction mixture was stirred for another 24 hours at room temperature. The product was washed with 3 × 20 ml of water to remove excess of catalyst. The dark green-bluish liquid was obtained when all solvent and excess of monomer was removed under vacuum and the reaction mixture was dried over drying agent. The polymer in the form of doped (0.32 FeCl₄⁻ per repeat unit) was precipitate out when it was washed with hexane and poured into cold methanol. The neutral dark brown polymer was formed by Soxhlet extraction with methanol and then treated by ammonium hydroxide and characterized by TLC. The resultant mixture was filtered and then dried under vacuum for 24 hours. Column chromatography (silica gel/petroleum ether) gave a brown neutral PHDTT powder with 56% yield. ¹H NMR (DMSO) δ 10.0 (sharp, s, aldehyde), 7.9, 7.3 (there were two broad peaks), 4.4 (br, m), 2.1, 1.8 (br, m), 1.1 (br, m); ¹³C NMR (DMSO)

(¹H decoupled) δ 184.7, 137.1, 130.5, 125.1, 113.7, 65.0, 30.3, 12.7; UV-VIS (CH₂Cl₂) λ_{max} 360 nm, IR (neat) 3238, 2871, 2775, 1821, 1629, 1439, 1366, 851, 779, 674 cm⁻¹. GPC 3000 g/mol. The PHDTT is soluble in DMF, CH₂Cl₂, and chloroform. ¹H NMR and ¹³C NMR spectrum of donor block is shown in Figure 2.

Acceptor Block PTFS

2, 5-Dibromo-3-Thiophene Carboxylic Acid, 2: 10.2 g (0.0797 mols) of 3-thiophene carboxylic acid, 1, was placed in a 500 mL round bottom flask equipped with a magnetic stirrer. 199.5 mL of glacial acetic acid was added. Then 22 ml (0.398 mols) of bromine was added gradually using a graduated addition funnel. The reaction was heated, stirred, and was carried out under reflux at 60°C in an oil bath overnight. TLC was used to monitor the reaction. After completion, light yellow crystal precipitate could be observed in an orange-yellow solution. The reaction mixture was placed in an ice bath and deionized water was added. Compound 2 is insoluble in water so crystals were formed and collected by vacuum filtration. The product, light yellow crystals, was then placed in a vacuum oven at \approx 40-60 °C and left overnight resulting in 20.08 g (88% yield) of compound 2. ¹H NMR (DMSO): δ 13.4 (s), 7.4(s). ¹³C NMR: δ 161.6, 133.1, 132.1, 118.3, 111.1. Anal. Calcd for C₅H₂O₂Br₂S: C, 21.00; H, 0.70. Found: C, 20.49; H, 0.71. Melting point was 170 °C (s).

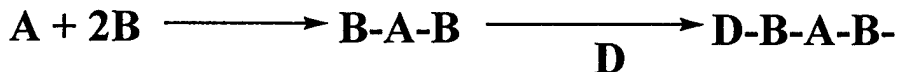
Heptafluorobutyl 2, 5-dibromo-3-thiophene carboxylate, 4i: 10.0 g (0.035mols) of 2, 5-dibromo-3-thiophene carboxylic acid, 2, were added to a 500 mL round bottom flask followed by 26 mL (0.35 mols) of thionyl chloride in excess. The reaction was stirred and refluxed overnight. After completion, a rotary evaporator was used to remove excess thionyl chloride. A light yellow/peach crystalline solid remained in the flask. Without any further purification process, 22 ml of pyridine was added to an addition funnel followed by 0.175 mols of *n*-heptafluorobutanol. The contents were then slowly added to the flask, refluxed and stirred at 80 °C overnight. A separatory funnel and CHCl₃ was used to extract the organic layer. A rotary evaporator was used to remove excess solvent. Column chromatography using silica and CHCl₃ as the mobile phase was carried out to separate the monomer from impurities. Excess CHCl₃ was removed via the rotary evaporator. The monomer was then removed from the flask. A light yellow solution remained. 9.34 g were recovered (57% yield) ¹H NMR (DMSO): δ 7.46 (s), 5.08 (t), ¹³C NMR (DMSO): δ 158.27, 131.24, 129.72, 121.35, 112.28, 59.61, 59.25, 58.91. Anal. Calcd. for C₉H₃Br₂F₇O₂S: C, 23.10; H, 0.65. Found: C, 23.17; H, 0.72.

Aldehyde End-Functionalized Polythiophene: 10.5 g (0.022 mols) of the monomer, heptafluorobutyl 2, 5-dibromo-3-thiophene carboxylate (4i), was added to a 500 mL round bottom flask equipped with a magnetic stirrer. 5.7 g (0.09 mols) of copper-bronze powder and 75 mL of anhydrous DMF was added to the flask. This was done in a glove box because of the air/moisture sensitivity of the catalytic copper powder. The ratio of 4i to copper was 1:4 respectively. For every mol of copper, about 800 mL of DMF was added. The reaction was refluxed and stirred at 190 °C, and the flow of dry N₂ gas allowed for an inert atmosphere. The reaction was carried out for three days. On the second day (after 24 hours of reaction), 6.16 mL (0.067 mols, excess amount) of 2-thiophene carboxyaldehyde

was added to terminate the polymer chains. TLC was done, and one spot would indicate the formation of the polymer. There were no monomer or terminator spots present. The reaction mixture was filtered via a series of filtering and makeshift flash silica gel chromatography to remove the copper powder, and the polymer was recovered, which was an orange-red powder-like solid.

Final Block Copolymer PT-FB: The synthesis of -BABD- type of polythiophene is as follows: The mixture of PHDTT with excess amount of 1,4-diamine butane in dry DMSO was allowed to stirred for 48 hours under reflux. Then the reaction was stopped, the mixture was precipitated in methanol and excess bridge was removed by water. ^1H NMR (DMSO) δ 2.7, 2.5 (m, 4H; m, 4H), 1.5 (m, 2H), 1.2 (m, 4H), 0.9 (m, 6H); GPC, 3200 g/mol. The -BDB- (bridge-donor-bridge) was then coupled with equal mole ratio of fluorinated acceptor in DMSO. The mixture was stirred in room temperature for 48 hours and was precipitated in methanol and washed with water. After repeated precipitation and drying the mixture, column chromatography (silica gel/hexane) was performed to obtain a dark red-brownish colored block copolymer. ^1H NMR (DMSO) δ 8.0, 7.6 (broad peak), 3.5, 3.4 (m, 4H), 1.7 (m, 2H), 1.4 (m, 2H), 1.2 (m, 6H), 0.9 (m, 8H); GPC, 18000 g/mol. Schematic structure of a -BABD- is shown in Scheme 2. Final block copolymer can have very small aldehyde terminator at the end of the polymer chain which it can not be detected by ^1H NMR as shown in Figure 7. Purification of final block copolymer is important as well as in each step of formation of block A or D to insure all mixture of compound with various end groups have been separated from final compounds. This produces a well-defined block polymer of A or D or A+D and the results can be confirmed with NMR integration of products.

The synthetic strategy of the final block copolymer is shown below: the acceptor block react with excess amount of bridge units to form -BAB- as intermediates, and then donor block can be added at the end. By building an electron rich donor block, an electron neutral bridge block, and an electron deficient acceptor block into D-B-A type block copolymer, one could actually maximize and minimize donor/acceptor interaction and optimize the photovoltaic efficiency at the same time in one system.



Either synthetic route will produce the polythiophene of final block copolymer (PT-FB). The alternative way of synthesizing final block copolymer is similar to first route with some changes such as using the appropriate solvent and temperature.^{7,10,19} It is important to note that end capped block polymers can facilitate formation of copolymer with given ability to control the size of nano-structured polymer easily, when exact mole ratio of donor or acceptor is used. This can be very useful to produce size tailored materials with exact units of desired copolymer. A research on this aspect of synthesizing copolymer of polythiophene is on going and will be reported in near future.