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Broadening Absorption in Conductive Polymers through Cross-linkable Side Chains in a Nonconjugated Polymer Backbone

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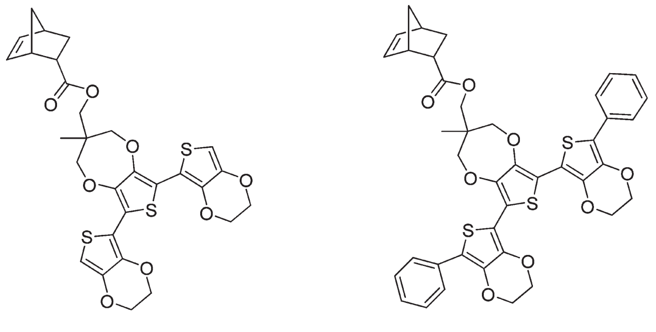
ABSTRACT: Novel nonconjugated copolymer precursors containing polymerizable triEDOT and nonpolymerizable diphenyl triEDOT at side chains were synthesized by the ring-opening metathesis polymerization (ROMP). Subjecting these polymers to oxidative conditions selectively cross-links the triEDOT units, while leaving the diphenyl triEDOT groups intact. The resulting cross-linked polymers exhibit broad absorption signals with tunable contributions from the diphenyl triEDOT oligomers and conjugated EDOT polymers.

Introduction

Conjugated polymers have been pursued with great interest due to its potential as electrically and/or optically active materials in applications such as electrochromics,[1] sensors,[2] thin film transistors,[3] light emitting diodes,[4] and photovoltaics.[5] The potential of these polymers will be greatly enhanced if these polymers are easily processable, because processability has significant implications in device fabrication. Although the optical and electronic properties of conjugated polymers are enhanced with greater degree of planarity and conjugation, solubility of these polymers in common organic solvents suffers most of the time.[6] Synthetic chemists often circumvent this by simply incorporating linear or branched alkyl side chains in these conjugated polymers.[7] While instilling solubility onto the polymers, these alkyl chains could have deleterious effects on the conducting properties of these polymers as well.[8] Also, a desirable feature of conjugated polymers is that the solubility of these polymers be modified after incorporation onto a surface. For example, when a soluble polymer is rendered insoluble after incorporation on to a surface, this facilitates the incorporation of additional materials over that surface without significantly disturbing the original polymer layer. In this context, flexible precursor polymers have been converted into insoluble conjugated polymers in the solid state.[9] Herein, we envisaged an approach that not only addresses the issues mentioned above, but also concurrently meets two other needs. To better match the high flux spectral region of the solar spectrum, low band gap polymers are of great interest in photovoltaics.[10] In a similar vein, it is also desirable that these polymers exhibit a broad absorption spectrum. We show here that our approach has the potential to simultaneously address these issues as well.

Several strategies have been reported in the literature to lower the band gap of conjugated polymers as well as to broaden the absorption spectral range of the chromophores.[11] For example, the absorption range of conjugated polymers has been expanded by incorporating side chain chromophores.[12] In this paper, we present a complementary method to render the polymer insoluble after incorporation on to a surface, red-shift the absorption spectrum of one part of the polymer, and thus concurrently broaden the absorption spectrum during the process. For this purpose, we have incorporated cross-linkable and noncross-linkable units as side chains of nonconjugated copolymers. Oxidative polymerization of these copolymer precursors causes the cross-linking of active units resulting in conjugated polymers, which exhibit absorption in the longer wavelength regions while the nonpolymerizable functionalities retain their spectral characteristics. To the best of our knowledge, utilizing polymers containing cross-linkable side chain units to broaden the absorption spectra has not yet been explored extensively.

Chart 1. Structures of 3,4-Dialkoxythiophene Trimer (1) and Its Phenyl-Capped Counterpart (2)



1 **2**

Results and Discussion

We targeted 3,4-dialkoxythiophene- (ADOT-) based polymer as the scaffold for our studies. Although poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits excellent optoelectronic properties, utility of this polymer in many application is limited to the more processable PEDOT−PSS blend. Therefore, we presume that a processable precursor polymer that would ultimately provide PEDOT analogues would be attractive. As mentioned above, our molecular design will contain an oligomeric precursor of the conjugated polymer as the side chain in a nonconjugated polymer backbone. Monomeric 3,4-ethylenedioxythiophene (EDOT) does not have a functional group handle to attach the polymerizable functionality. Therefore, we targeted a 3,4-dialkoxythiophene trimer (triADOT, represented by structure **1** in Chart 1) as the target monomer. In this structure, we have incorporated the free hydroxyl functionality of the proDOT monomer as the handle to attach to a norbornene-based monomer. The norbornene functionality will be used to

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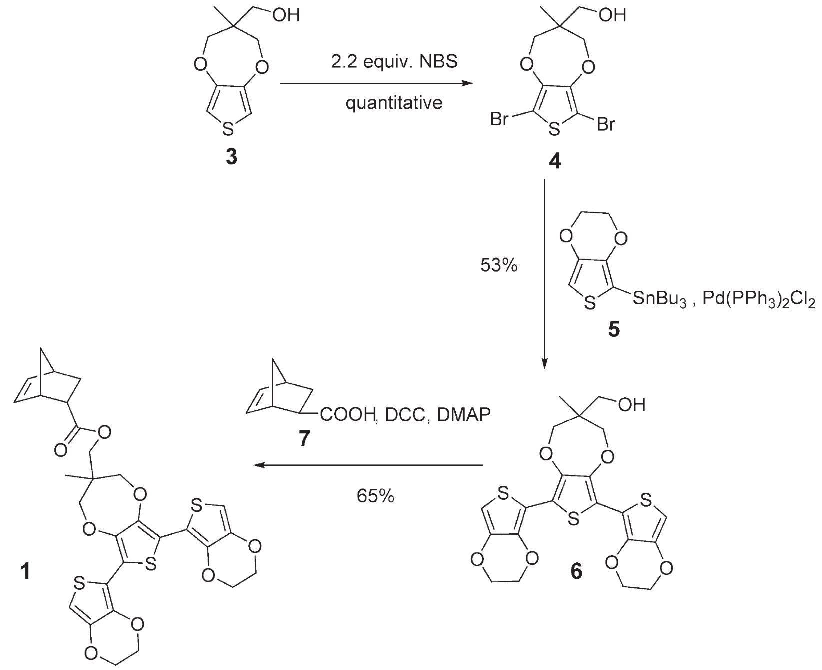
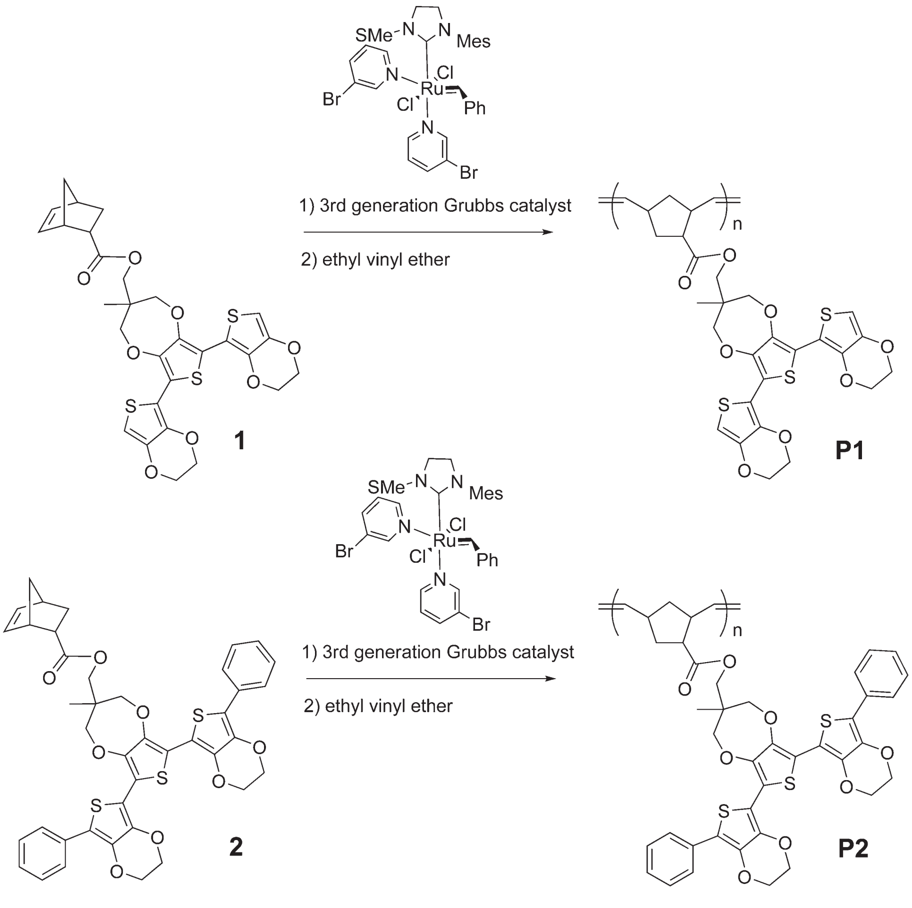
Scheme 1. Synthesis of Norbornene-Based Monomers Containing triADOT Derivatives as Side Groups



Scheme 2. ROMP Polymerization of Monomers 1 and 2



synthesize the processable polymer using ring-opening metathesis polymerization (ROMP), while the 2- and 5-positions of the flanking EDOT monomers in the trimer will be utilized for producing a conjugated polymer structure during the cross-linking step.

When the polymer of molecule **1** is subjected to cross-linking by polymerization of the side chain, polyADOT will be generated concurrently in the insoluble film. This extended conjugation in the monomer should result in a red-shift of the absorption spectrum of the polymer. To broaden the absorption spectrum of the polymer, we will only partially extend the conjugation of the oligomeric side chain. To predictably retain a percentage of the side chain oligomer, we envisioned capping the 2- and 5-positions of the triADOT monomer with phenyl rings. Structure of the phenyl capped triADOT containing norbornene monomer is shown in Chart 1 as structure **2**. Norbornene substituted EDOT derivative monomers were prepared in three simple steps. First, ProDOT (**3**) was converted to 2,5-dibromoProDOT **4** using *N*-bromosuccinimide. Compound **4** was then treated with the monotributylstannyl-substituted EDOT derivative **5** under palladium-catalyzed Stille coupling conditions to obtain desired the triADOT molecule **6** in 53% yield. Reaction between the hydroxyl group of compound **6** and the carboxylic acid functionality of 5-exonorbornene-2-carboxylic acid (**7**) in the presence of DCC/DMAP provided the targeted monomer **1**, as shown in Scheme 1. Similar reaction using monophenyl−monostannyl EDOT molecule provided the targeted monomer **2**.[13]

First, we synthesized the homopolymers from monomers **1** and **2**. ROMP was preformed using the third generation Grubbs catalyst under inert atmosphere in dry THF. We observed that the polymerization happened readily in a few minutes and the reaction was terminated using ethylvinylether (Scheme 2). The molecular weight of the polymers **P1** and **P2** (from monomers **1** and **2** respectively) were found to be about 13K and 10K with a PDI of 1.04 and 1.10 respectively, as shown in Table 1. Thermal stability of **P1** and **P2** was evaluated using thermogravimetric analyses (TGA). Polymers **P1** and **P2** exhibit good thermal stability with the decomposition onset temperature of ca. 390 °C. Differential scanning calorimetric (DSC) measurements were also performed. The T_g of **P1** and **P2** was found to be about 182 and 197 °C, respectively.

Table 1. Characteristics of All Copolymers Obtained from Monomers 1 and 2

polymer	monomer **1**:monomer **2**	monomer:catalyst	$M_n{}^a$ (g/mol)	PDI
P1	1:0	40:1	12.8K	1.04
P2	0:1	40:1	10.0K	1.10
P3	3:1	100:1	16.8K	1.06
P4	1:1	100:1	23.5K	1.08
P5	1:3	100:1	16.8K	1.10

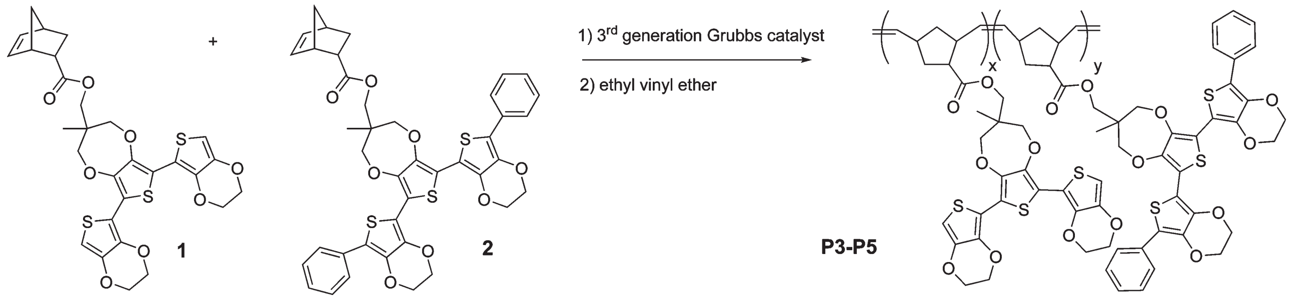
[a] M_n values are estimated based on the PMMA standards.

To achieve the targeted broad absorption spectrum by cross-linking only part of the polymer, copolymers with different ratios of monomers **1** and **2** were synthesized under the same polymerization conditions used for the homopolymer synthesis, as shown in Scheme 3. The characteristics of the copolymers are shown in Table 1.

Spectroelectrochemistry

The polymers **P1**−**P5** were all found to be soluble in most common organic solvents, thereby endowing facile film-casting capabilities on to these polymers on any substrate. In order to investigate the electrochemical behaviors of the homopolymers **P1** and **P2**, containing triADOT and diphenyl triADOT groups as pendents respectively, the polymers were cast on to an ITO coated glass and examined using spectroelectrochemistry. Figure 1 shows the spectroelectrochemistry of **P1** in 0.1 M (TBA)PF_6/ACN. Polymer **P1** exhibits an absorption spectrum with a wavelength range of 350−430 nm. Upon applying a potential of 800 mV to this film, the absorption signal at 350−430 nm reduces significantly with the concurrent appearance of a peak around 850 nm. The lack of any new peak within the spectral range examined suggests that under the applied potential, we have polymerized the triADOT side chain in reasonably high yields and thus cross-linked the polymer. Further oxidation of the product polymer under the applied potential, one would expect the formation of radical cations and/or dications of the polyADOT product. The absorption of such a dications is expected to be in the near-IR region. If this were indeed true, reduction of the cations and dications by applying a reduction potential would result in an absorption spectrum of the polymer that corresponds to the neutral polyADOT polymer (Scheme 4 and Figure 1a).

Scheme 3. Copolymerization of Monomers 1 and 2 in Different Ratios



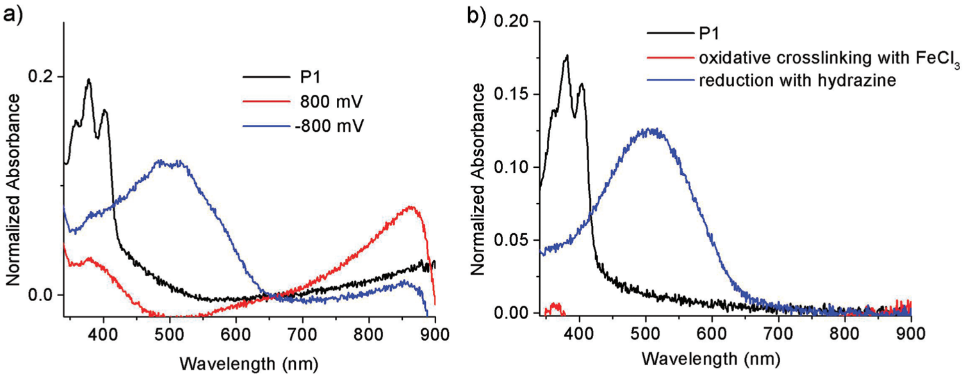
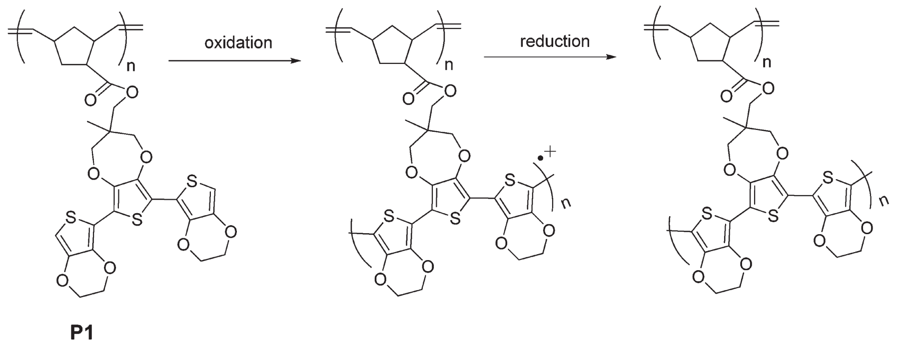
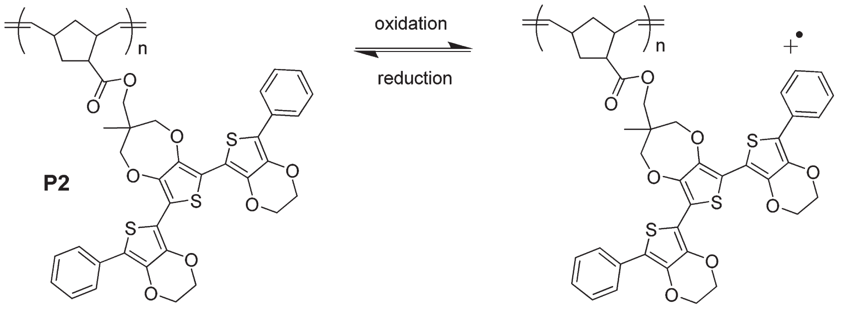


Figure 1. Electrochemical (left) and chemical (right) cross-linking of **P1**.

Scheme 4. Oxidative Polymerization of P1 and Reduction of the Cross-Linked P1



Scheme 5. Proposed Mechanism for a Redox Reaction of P2



Upon applying a potential of −800 mV, a broad spectrum with absorption ranging 350−680 nm was observed. This spectrum is close to that observed for PEDOT, which suggests that we have indeed cross-linked the polymer film and synthesized polyADOT in situ. We also observed that (i) the original absorption spectral characteristics at 350−430 nm were not recovered upon applying a reducing potential and (ii) the film is insoluble, suggesting that cross-linking has occurred.

We were also interested in identifying whether the redox reactions above can be achieved using chemical oxidants, because such oxidative coupling reactions are often faster. To test this possibility, a film of **P1** was dipped in to a solution of $FeCl_3$ in acetonitrile. The absorption spectrum of the resultant film is indicative of the oxidative coupling induced polymerization of the side chain. Reduction of the cross-linked polymer to a neutral structure was then achieved by subsequently dipping the cross-linked film into hydrazine solution in acetonitrile. The spectroscopic signature obtained after this step is consistent with the formation of polyADOT, as observed with the electrochemical cross-linking method (Figure 1b).

Similarly, since the 2- and the 5-positions of the thiophenes are capped by phenyl groups in **P2**, it is expected that applying a potential will not result in cross-linking or polymerization. In this case, applying a positive potential of 800 mV should afford stable monocations or dications. Upon subjecting to a reducing potential of −800 mV to this film should completely reverse the cationic side chains to the neutral polymer **P2** without cross-linking (Scheme 5). We were gratified to find that this was indeed the case. The spectroelectrochemistry of **P2** under the oxidizing and reducing potentials are shown in Figure 2. Upon subjecting to a 800 mV potential, the original absorption signal of **P2** disappears accompanied by the emergence of a new absorption at 500−700 nm. This peak is attributed to the radical cation of the phenyl capped triADOT. The reductive potential at −800 mV causes the reappearance of the original signal at 350−500 nm. These results show that the phenyl capping indeed prohibit the oxidative cross-linking at α positions of the triADOT units.

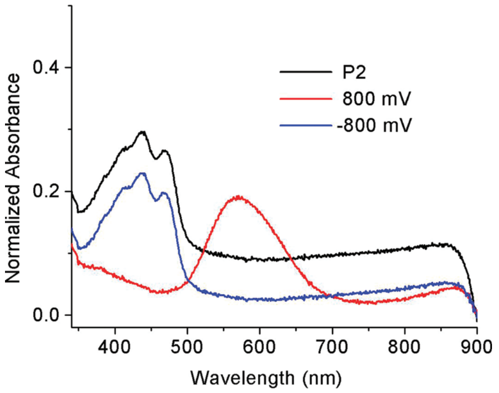


Figure 2. Spectroelectrochemistry of **P2** under oxidation and reduction conditions.

Broadening the Absorption Spectra in Cross-Linked Copolymer Films. Considering that **P1** provides a red-shifted spectrum upon subjecting to the redox reactions and that **P2** does not get affected, we envisioned the possibility that the copolymers would exhibit a blend of the two spectra. Moreover, the relative intensities in the blue vs red region can be controlled by simply tuning the ratio of the monomers **1** and **2** in the polymer. We tested these possibilities with three different copolymers **P3**−**P5**, shown in Table 1. These copolymer films were prepared by spin coating the polymers on a glass slide. Chemical cross-linking of these copolymers in solid state was carried out using iron(III) chloride as an oxidant. The color of all thin films changed from their original yellow color to an intense blue color indicating the cross-linking of these copolymers. The films were washed with acetonitrile to remove any adsorbed iron(III) chloride, before dipping the film into a solution of hydrazine in acetonitrile to reduce the oxidized and cross-linked polyADOT copolymer film. At this juncture, the film color

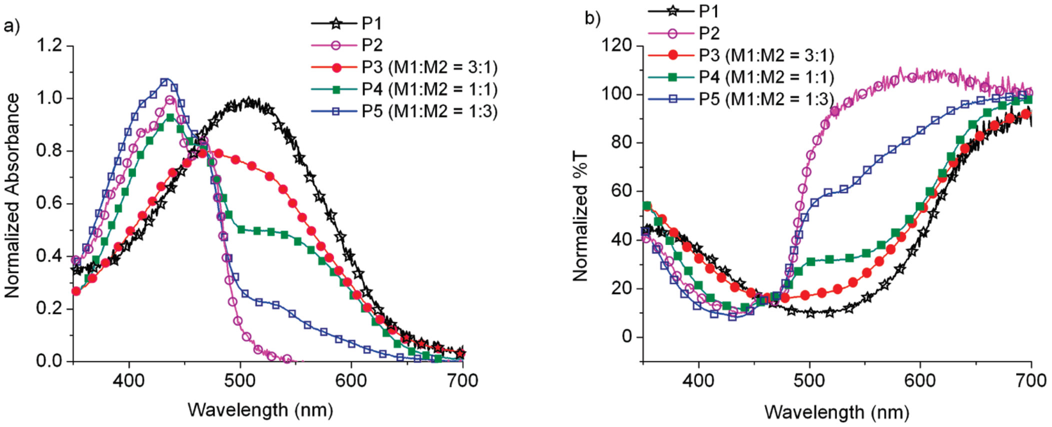


Figure 3. Normalized (a) absorption spectra of cross-linked copolymer **P1**−**P5** and (b) transmittance plot of polymers **P1**−**P5**.

changed from blue to brown as expected. The absorption spectra of the films also indicated successful reduction of the cross-linked films to neutral polyADOT structures. The spectral characteristics of the final polyADOT cross-linked copolymer films are shown in Figure 3. The copolymers **P3**−**P5** exhibit both the absorption characteristics of the cross-linked **P1** in the long wavelength region and that of the un-cross-linked **P2** in the short wavelength region. In addition to combining the spectral characteristics and thus cover a broad spectrum, it also should be noted that the relative intensities of absorption in the blue and red regions could be tuned by simply modifying the monomer ratios (Figure 3).

Conclusions

We have synthesized norbornene-based polymers that contain dialkoxythiophenes as pendant side chains as an approach to processable precursors to insoluble conjugated polymers. When the 2- and 5-positions were uncapped, subjecting the polymer to chemical or electrochemical oxidation reaction provides cross-linked films. When these positions are capped with phenyl rings, the polymer thin film does not cross-link. The cross-linking process concurrently results in red shift in absorption spectrum of the polymer. Thus, when copolymers are synthesized with the uncapped and capped oligothiophenes, oxidative polymerization of these films provide a broad absorption spectrum. The relative intensities in the blue and the red regions of these films can be tuned by simply varying the percentage of the two monomers in the copolymer. We recognize that the chosen side chains and the resultant absorption spectra are not optimized yet to match the solar spectrum. However, we expect that the design strategy outlined here will have implications in the future design of processable conjugated polymers in optoelectronic applications, such as electrochromic materials and photovoltaic devices.

Experimental Section

General Experimental Details. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 and 100 MHz NMR spectrometer using the residual resonance of the solvent as internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; d of d, doublet of doublet; m, multiplet, br, broad. UV−visible spectra were obtained from a Cary 100 spectrophotometer. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) using PMMA standard with a refractive index detector. The THF was distilled over sodium/benzophenone. third generation Grubbs catalyst,[14] 3,4-propylenedioxythiophene derivative (ProDOT)[15] (**3**), 2-tributyltin EDOT[16] (**5**) and 2-phenyl EDOT[17] (**8**) were prepared according to the literature procedure. All other chemicals were obtained from commercial sources and used without any other purification unless otherwise stated.

Synthesis of 2,5-Dibromo ProDOT (4). In a two-necked 250 mL round-bottom flask filled with 20 mL of chloroform was added 0.60 g (3.00 mmol) of ProDOT (**3**), and the solution was bubbled under argon for 20 min. Then, 1.11 g (9.00 mmol) of *N*-bromosuccinimide (NBS) was added and the mixture was stirred for 20 h. After completion of the reaction, the solvent was removed and the resulting residue was purified by column chromatography using 100% CH$_2$Cl$_2$. The product was obtained as a white solid with quantitative yield. ^{1}H NMR ((CD$_3$)$_2$CO, δ, ppm): 4.00 (d, 2H, J = 12.0 Hz), 3.73 (d, 2H, J = 12.0 Hz), 3.60 (s, 2H), 0.97 (s, 3H). ^{13}C NMR ((CD$_3$)$_2$CO, δ, ppm): 147.8, 90.8, 76.9, 63.7, 43.7, 16.1

Synthesis of TriADOT Derivative (6). To a two-necked 50 mL round-bottom flask were added 0.50 g (1.40 mmol) of 2,5-dibromo ProDOT (**4**) and 1.32 g (3.07 mmol) of 2-tributyltin EDOT (**5**) in DMF (50 mL). The mixture was deaerated several times before handled under argon. Then, 0.07 g (0.10 mmol) of Pd(PPh$_3$)$_2$Cl$_2$ was added and the mixture was stirred at 80 °C for 2 h. After completion of the reaction, water was added and the mixture was extracted using CH$_2$Cl$_2$ (3 × 20 mL). Organic layers were collected and dried over anhydrous MgSO$_4$. The resulting residue was purified by column choromatography using 50% ethyl acetate in dichloromethane. The product was obtained as a yellow solid with 53% yield. ^{1}H NMR (CDCl$_3$, δ, ppm): 6.24 (s, 2H), 4.33 (s, 4H), 4.21 (br, 6H), 3.85 (br, 2H), 3.75 (br, 2H), 0.96 (s, 3H). ^{13}C NMR (CDCl$_3$, δ, ppm): 145.2, 141.0, 137.2, 112.8, 109.7, 97.6, 76.9, 65.5, 64.2, 63.5, 43.5, 15.6

Synthesis of Diphenyl TriADOT Derivative (9). 2-Phenyl-5-tributyltin EDOT (**10**) was prepared according to the following procedure. First, 1.00 g (4.58 mmol) of 2-phenyl EDOT (**8**) was dissolved in dry THF (20 mL). At −78 °C, 5.70 mL (9.16 mmol) of *n*-BuLi was slowly added and the reaction temperature was maintained at −78 °C under strong stirring for 1 h before 2.84 mL (10.53 mmol) of Bu$_3$SnCl was subsequently added. The mixture was heated up to room temperature and left stirring overnight. After completion of the reaction, the solvent was removed by a rotary evaporator. The residue was dissolved in hexanes and filtered. The filtrate was dried under vacuum to afford the product **10** as an oily liquid which was further used in the next step without further purification. ^{1}H NMR (CDCl$_3$, δ, ppm) 7.74 (br, 2H), 7.39−7.31 (br, 2H), 7.20 (br, 1H), 4.33−4.27 (m, 2H), 4.25−4.19 (m, 2H), 1.73−1.49 (m, 16H), 1.46−1.25 (m, 16H), 1.23−1.02 (m, 16H), 1.00−0.86 (m, 12H). ^{13}C NMR (CDCl$_3$, δ, ppm) 148.3, 138.3, 133.4, 128.2, 126.2, 125.1, 123.1, 106.6, 69.5, 29.1, 27.3, 13.8, 10.4

To a two-necked 50 mL round-bottom flask were added 0.50 g (1.36 mmol) of 2,5-dibromo ProDOT (**4**) and 1.52 g

(2.99 mmol) of 2-phenyl-5-tributyl tin EDOT (**10**) in DMF (50 mL). The mixture was deaerated several times and then handled under argon. 0.07 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$ was added and the mixture was stirred at 80 °C for 2 h. After completion of the reaction, water was added and the mixture was extracted using CH_2Cl_2 (3 × 20 mL). Organic layers were collected and dried over anhydrous $MgSO_4$. The resulting residue was purified by column choromatography using 10% ethyl acetate in dichloromethane. The product was obtained as a yellow solid with 17% yield. ^{1}H NMR ($(CD_3)_2CO$, δ, ppm) 7.74 (br, 4H), 7.39 (t, J = 7.7, 4H), 7.22 (br, 2H), 4.45 (s, 8H), 4.25 (d, J = 11.9, 2H), 3.91 (d, J = 11.9, 2H), 3.78 (d, J = 6.0, 2H), 1.07 (s, 3H). ^{13}C NMR ($(CD_3)_2CO$, δ, ppm): 144.1, 128.6, 126.2, 125.5, 76.3, 64.9, 63.0, 43.5, 15.9

Synthesis of 5-Norbornene-*exo*-2-triADOT Carboxylate (1). A 0.10 g (0.21 mmol) sample of triADOT (**6**) and 0.06 g (0.43 mmol) of 5-exonorbornene-2-acetic acid (**7**) were dissolved in dry THF, and the mixture was cooled down to 0 °C. Then 0.09 g (0.43 mmol) of dicyclohexyl carbodiimide (DCC) and 0.05 g (0.43 mmol) of 4-dimethyl aminopyridine (DMAP) were added to the mixture portionwise. The mixture was stirred at 0 °C for 2 h. After completion of the reaction, the precipitated dicyclohexyl urea was filtered. Then, water was added and the mixture was extracted using CH_2Cl_2 (3 × 20 mL). Organic layers were collected and dried over anhydrous $MgSO_4$. The resulting residue was purified by column choromatography using 30% ethyl acetate in hexanes. The product was obtained as a yellow solid with 65% yield. ^{1}H NMR ($CDCl_3$, δ, ppm) 6.29 (s, 2H), 4.37 (br, 4H), 4.31 (br, 1H), 4.27 (br, 4H), 4.21 (br, 1H), 3.87 (br, 2H), 3.10 (br, 1H), 2.96 (br, 1H), 2.33−2.28 (br, 1H), 1.96 (br, 1H), 1.43 (br, 3H), 1.07 (s, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 176.2, 143.8, 141.0, 137.9, 137.2, 135.2, 113.1, 97.6, 66.3, 64.9, 64.2, 46.6, 43.1, 41.4, 33.9, 30.4, 16.6.

Synthesis of 5-Norbornene-*exo*-2-diphenyl triADOT Carboxylate (2). Similar to the procedure for 5-norbornene-exo-2-triADOT (**1**), 0.10 g (0.16 mmol) of diphenyl triADOT (**9**), 0.04 g (0.32 mmol) of 5-exonorbornene-2-acetic acid (**7**), 0.05 g (0.32 mmol) of DCC, and 0.04 g (0.32 mmol) of DMAP were employed. The crude product was purified by column chromatography using 30% ethyl acetate in hexanes. The product was obtained as a yellow solid with 69% yield. ^{1}H NMR ($CDCl_3$, δ, ppm) 7.72 (br, 4H), 7.44 (br, 4H), 7.29 (br, 2H), 6.22 (br, 2H), 4.47 (d, J = 12.9, 8H), 4.36−4.22 (m, 4H), 3.96 (d, J = 9.6, 2H), 3.13 (br, 1H), 2.96 (br, 1H), 2.37 (br, 1H), 1.96−1.89 (m, 1H), 1.28 (br, 3H), 1.05 (s, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 176.5, 135.8, 128.6, 126.3, 124.8, 69.7, 66.6, 64.5,46.2, 43.1, 41.1, 30.4, 16.6

Syntheses of Polymers P1−P5 by Copolymerization of Monomers 1 and 2. Dry THF was taken into a round-bottom flask and was subjected to freeze−pump−thaw cycle 3 times before use. The mixture of 1:0, 0:1, 3:1, 1:1, and 1:3 ratios of monomers **1** and **2** and third generation Grubbs catalyst were put under vacuum into two separated round-bottom flasks for 30 min before THF was added. Then, the solution of monomers in THF was injected into a stirred solution of the catalyst. The mixture was allowed to stir for 3 min at room temperature followed by irreversible termination via the addition of 2 mL of ethyl vinyl ether. The solution was then concentrated under vacuum. The polymers were obtained by precipitating the mixture twice in either methanol or ether. The precipitants were collected and dried *in vacuo* to yield polymers as yellow solid. ^{1}H NMR ($CDCl_3$, ppm) δ 7.81−7.61 (br, 4H), 7.26 (br, 6H), 6.30−6.05 (br, 2H), 5.50−4.88 (br, 4H), 4.27 (br, 24H), 3.92−3.54 (br, 4H), 3.19−2.79 (br, 4H), 2.79−2.28 (br, 2H), 2.28−1.67 (br, 8H), 1.33−0.69 (br, 6H).

Cross-Linked P1 and P2 by Oxidative Electropolymerization. P1 and **P2** in dichloromethane were spun-coat onto ITO-coated glass, and electropolymerization was performed in 0.1 M tetrabutyl ammonium hexafluorophosphate ($(TBA)PF_6$) in acetonitrile by repeated scanning between −800 and +800 mV at a scan rate of 100 mV/s.

Chemical Cross-Linking of P1−P5 Using $FeCl_3$ Followed by Hydrazine. Polymers in dichloromethane were spun-coat on a glass slide at a rate of 1000 rpm. The cross-linking of polymers were preformed by dipping the film into an acetonitrile solution containing 0.01 M $FeCl_3$ for a few minutes. Then, the film was washed with acetonitrile before it was dipped into 0.005 M hydrazine in acetonitrile for a few minutes. The film was washed with acetonitrile and dried before recording the absorption spectrum.

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Supporting Information Available: Text giving synthetic and other experimental details, drawings of structures of the compounds, and figures showing TGA and DSC curves and absorption spectra of **M1** and **M2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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