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Processable, Regioregular, and "Click"able Monomer and Polymers Based on 3,4-Propylenedioxythiophene with Tunable Solubility

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ABSTRACT: "Click"able monomer and polymers based on 3,4-propylenedioxythiophene, ProDOT, which can be functionalized either at the monomer stage or after the polymerization, were synthesized and characterized for the first time. The solubility of these polymers can be fine-tuned from organic to aqueous solvents by functionalization with an appropriate side chain. In fact, the "click"able functionality allows us to synthesize and chatacterize water-soluble ProDOT-based cationic polymer which were hitherto unknown. Chemical polymerization of propargyl-functionalized ProDOT (ProDOT-propargyl) resulted in an insoluble polymer which could be made water-soluble by reacting it with 1-azido-ethanoic acid sodium salt or 3-azidopropyltrimethylammonium iodide using "click" chemistry. Interestingly, the chemical copolymerization of ProDOT-propargyl with 25 mol % of dihexyl-ProDOT resulted in an organic soluble polymer which was characterized using NMR, FTIR, UV–vis spectroscopy, solution doping, and GPC. This polymer was then used successfully for "click" chemistry in solution. The "click" reaction that was performed on this polymer by using 2-azidoacetic acid sodium salt or 3-azidopropyltrimethylammonium iodide resulted in the complete reversal of solubility from organic solvent of the parent polymer to water solubility of the resulting polymers. In order to study the electrochemical properties, thin films of poly(ProDOT-propargyl) were prepared using electrochemical polymerization and were characterized by electrochemical, spectrochemical, optical switching, and in situ conductance measurements. Electropolymerization resulted in the formation of an electroactive film on the electrode surface. Spectroelectrochemical studies indicated that the polymer switched from opaque blue to a transmissive oxidized state with a contrast of 75%. In situ conductance studies showed a maximum conductance of 0.03 S.

Introduction

Polymers based on 3,4-alkylenedioxythiophenes are of special interest due to their low oxidation potential, high thermal and chemical stability in the doped state, high transparency in the doped state, ability to act as hole transport layer in light-emitting devices, and also in the design and fabrication of chemical and biological sensors.[1] Among the various derivatives of 3,4-alkylenedioxythiophenes, 3,4-ethylenedioxythiophene (EDOT) is the most widely studied one and is also available in bulk quantities in the monomeric form as well as in the water-dispersible polymeric form (PEDOT). Zhang et al. used polyaniline nanofibers coated with PEDOT using oxidative polymerization route resulting in the formation of a bilayer nanostructured composite.[2] This nanocomposite exhibited better electrochemical properties compared to that of the parent PANI nanofibers. Letaief et al. synthesized and characterized a nanocomposite based on PEDOT and clay.[3] Shallcross et al. reported the use of PEDOT for the synthesis of nanocomposite thin films based on PEDOT–semiconductor nanoparticles which were then tethered to indium tin oxide substrate via electropolymerizaiton.[4] Sun et al. used poly(acrylic acid) for the polymerization of EDOT resulting in the synthesis of water-dispersible PEDOT–PAA composites.[5] Im et al. reported a novel oxidative chemical vapor deposition (oCVD) for the syntheses of thin films of PEDOT with controlled thickness and electrochemical properties.[6] Ocafrain et al. observed that it is possible to enhance effective conjugation length via the polymerization of preorganized monomers.[7] They used a hybrid system based on EDOT–thiophene to form self-assembled monolayers which upon electropolymerization resulted in polymers with enhanced conjugation length as well as transport properties. Nielsen et al. reported acrylate-functionalized discrete oligomers based on thiophene/EDOT/phenylene for photopatterning.[8]

Various efforts have also been directed toward the syntheses of polymers based on 3,4-alkylenedioxythiophenes. Zong et al. used double Mitsunobu reaction as the key step for the synthesis of various EDOT and ProDOT derivatives. Balog et al. reported the synthesis of a functional EDOT derivative bearing a highly nucleophilic thiolate group as the side chain.[9] They demonstrated that it is possible to carry out chemical modifications of this functional monomer both at the monomer stage and after the polymerization. Sotzing and co-workers explored the use of various nonconjugated soluble polymers with pendant EDOT groups to prepare thin films which were then converted to conducting films by the solid state polymerization of the pendant EDOT derivatives.[10] Reeves et al. reported a novel way to process ProDOT-based polymers using defunctionalization route.[11] They used a soluble polymer which can be converted into an insoluble polymer via chemical modification of the pendant side chain.

Despite a lot of interest in developing newer applications based on existing PEDOT, progress on the synthesis and characterization of new structural derivatives remains sluggish. This is due to the difficulties in the tedious multistep synthetic strategies adopted so far.[12] A solution to this problem could be in the design and synthesis of a suitable monomer which can act as a starting point for structural modifications both at the monomer stage or after the polymerization. Furthermore, a synthetic approach would be much more attractive if structural modification can be carried out without protection/deprotection strategy. In this direction, "click" chemistry[13] provides an attractive solution and has been used extensively for the synthesis of bioactive molecules such as DNA, sugar (oligosaccarides), proteins, and peptides.[14] The yield and specificity of the "click" reaction makes it an important and efficient route

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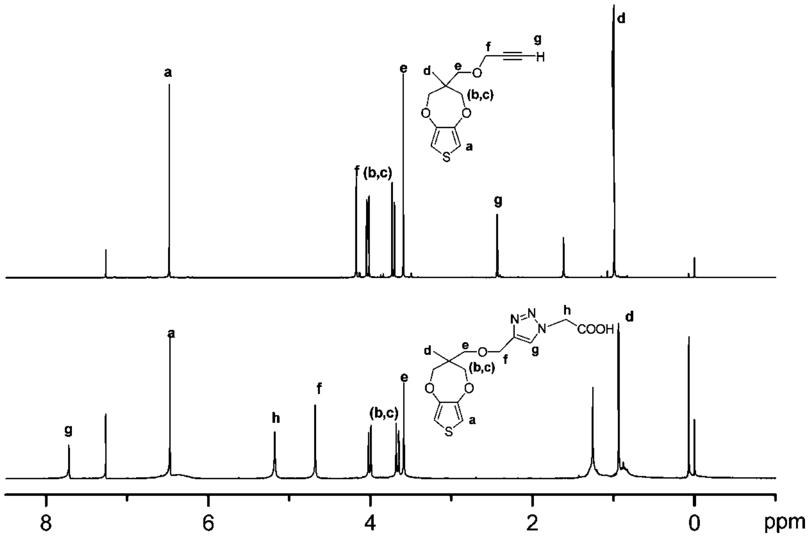
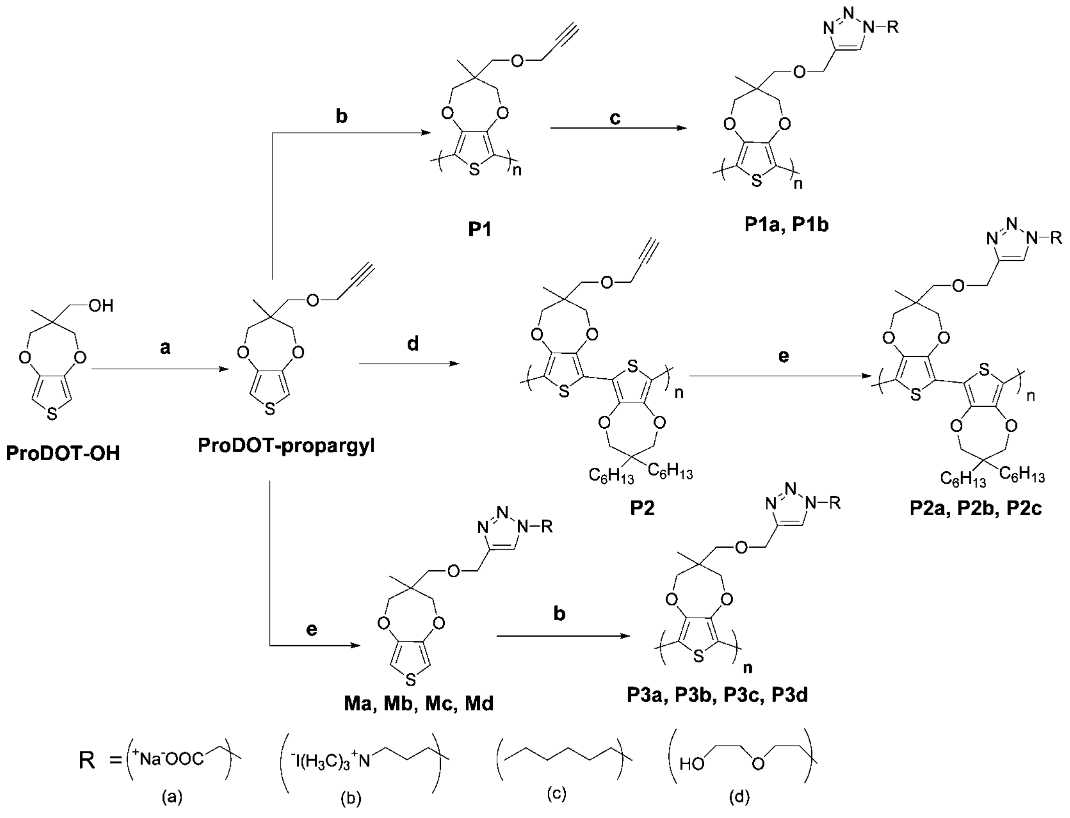


Figure 1. ^{1}H NMR of the "click"able monomer, 3-methyl-3-prop-2-ynyloxymethyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepine (Pro-DOT-propargyl), and "click"ed monomer [4-(3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepin-3-ylmethoxymethyl)-1,2,3-triazol-1-yl]acetic acid (**Ma**).

Scheme 1. Synthetic Routes for "Click"able Monomers and Polymers



a) Propargyl tosylate, NaH, DABCO, THF; b) i: $FeCl_3$, $CHCl_3$ ii: $NH_2NH_2H_2O$ c) RN_3, DMSO/H_2O, $CuSO_4.5H_2O$, Sodium Ascorbate;
d) i: dihexyl ProDOT, $FeCl_3$, $CHCl_3$ ii: $NH_2NH_2H_2O$ e) RN_3, Acetone/H_2O, $CuSO_4.5H_2O$, Sodium Ascorbate, 80° C.

not only for the synthesis of small molecules but also for functionalization of polymers.[15−17]

Following this approach, we chose ProDOT-propargyl as the "click"able monomer which can be reacted with various azide-functionalized compounds both at the monomer stage and after polymerization. While our work was in progress, two reports appeared in the literature on "click"able EDOT. Interestingly, both these reports utilized azide-functionalized EDOT which was electropolymerized and then functionalized in solid state via "click" chemistry. The unsymmetrical nature of azide-functionalized EDOT (chemically different 2- and 5-positions of the thiophene ring) resulted in a polymer that was regiorandom in nature as it can have head to head, head to tail, and tail to tail coupling along the polymer main chain. It is well-documented in the literature that the electrochemical properties can be improved by the design of regioregular polymers (polymers based on thiophene having either head to tail linakges or monomers with chemically equivalent 2- and 5-position) compared to the corresponding regiorandom polymers.[18] Therefore, we report a system that, apart from giving a regioregular polymer, has many inherent advantages over the reported ones in terms of fine-tuning of solubility of the final polymers and scalability due to chemical polymerization. Furthermore, the selection of terminal acetylenic unit on the polymeric backbone is more attractive than the terminal azide unit because it introduces more diversity due to the ease of synthesis of azide-functionalized molecules compared to the corresponding acetylene-functionalized molecules. In this article we report on the synthesis and characterization of this new series of regioregular "click"able monomer and polymers based on acetylenic functionalized ProDOT.

Results and Discussion

ProDOT-propargyl was easily synthesized in a single step with a reasonably good yield (~50%) by O-alkylation of the hydroxymethyl-substituted ProDOT (ProDOT-OH) with propargyl tosylate using 1,4-diaza-bicyclo[2,2]octane (DABCO) as the catalyst (Scheme 1). It should be noted that O-alkylation of ProDOT-CH_2OH is not trivial due to the β,β-disubstituted nature of the hydroxyl group. Only alkylations with benzyl halides[9] and alkyl halides[10] (works only in DMF solvent) have been reported successfully until now, and these reaction conditions do not work when the other alkylating agents such as allyl halides, propargyl halides, and propane sultone are used. Interestingly, the presence of a catalytic amount of DABCO allows these reactions to be carried out with different alkylating agents in various solvents. The use of DABCO is essential for the success of O-alkylation of the hydroxyl group of ProDOT-OH as it opens up various avenues for the simple one-step syntheses of regioregular functional monomers based on ProDOT-OH. ProDOT-propargyl was isolated as a light yellow viscous liquid and was characterized by NMR, FTIR, and HRMS. ProDOT-propargyl was then used for "click" chemistry and was functionalized with carboxylate, ammonium, glyme, and alkyl side chains. The corresponding azides were used as "click" partners in the presence of copper sulfate and sodium ascorbate in acetone/water as the solvent system (Scheme 1). The progress of the "click" reactions was monitored by FTIR spectroscopy by the disappearance of the strong azide peak at 2109 cm^{-1}. The FTIR spectra of the "click"ed monomer also showed the absence of the acetylenic stretching frequency at 2390 cm^{-1}. The success of "click" chemistry was further confirmed by the appearance of the peak at 7.7 ppm in ^1H NMR due to a triazole proton and disappearance of the acetylenic proton peak at 2.4 ppm (Figure 1). The final "click"ed monomers were also fully characterized by NMR, FTIR, and HRMS. This clearly demonstrates the novelty of our approach that a single monomer, ProDOT-propargyl, can act as the starting point to get monomers with diverse functionalities with good yields in single step without a protection/deprotection strategy.

It could be advantageous if a single polymer instead of a single monomer can be used as the starting point to introduce various chemical functionalities on the backbone in a single step with a good yield. To demonstrate this, ProDOT-propargyl monomer was subjected to oxidative polymerization in chloroform using ferric chloride as an oxidant. The polymerization proceeded in the usual fashion wherein color change from light yellow to light green to dark blue with time was observed. Polymer **P1** was isolated by precipitating the reaction mixture in methanol followed by stirring it with hydrazine hydrate to undope the polymer. The resulting undoped polymer was isolated as a dark blue powder and was found to be insoluble in common organic solvents. Interestingly, although the polymer with propargyl as the side chain was insoluble, "click" chemistry could still be performed in the solid state to get soluble polymers. Hence, the insoluble polymer, **P1**, was reacted either with azidoacetic acid or 3-azidopropyltrimethylammonium iodide in dimethyl sulfoxide/water as the solvent in presence of copper sulfate. This resulted in the synthesis of water-soluble polyanionic (with carboxylate side chains), **P1a**, as well as polycationic (with ammonium side chains), **P1b**, conjugated polymers based on 3,4-propylenedioxythiophene. In fact, this is the first successful report wherein a cationic polyelectrolytic system based on ProDOT has been synthesized.

These polycationic conjugated systems based on ProDOT opens up new areas of research such as fabrication of all organic devices using layer by layer deposition with known polyanionic ProDOT. The final water-soluble polymers show the absence of acetylenic stretching frequency at 2329 cm^{-1} in FTIR spectra. Surprisingly, all our attempts to get a well-defined ^1H NMR solution spectra of **P1a** in D_2O or mixture of d_6-DMSO and D_2O with reasonable resolution were not successful. This is in agreement with other cases of conjugated polyelectrolytes.[11] Interestingly, in case of **P1b**, although the ^1H NMR spectra was not very well resolved, a peak at 8.1 ppm, due to a triazole proton, was observed when a mixture of d_6-DMSO and D_2O was used as solvent. This further confirms the success of "click" reaction. Furthermore, the polymeric nature of the resulting polymers was confirmed by UV−vis spectroscopy and GPC. The UV−vis spectra showed an absorption maxima at 571 nm for the polyanionic system (**P1a**) and at 582 and 635 nm for the polycationic system (**P1b**) that are typical of the $\pi-\pi^*$ transition in soluble 3,4-propylenedioxythiophene-based polymers. GPC (in water using sodium salt of polystyrenesulfonate as standards) showed a weight-average molecular weight of 4900 Da (PD of 1.44) for polyanionic (**P1a**) and 4000 Da (PD of 1.51) for polycationic (**P1b**), confirming the polymeric nature of the final product.

In order to explore the full potential of the "click" chemistry on these conjugated polymers based on ProDOT, it was desirable to get a soluble "click"able polymer. This was easily achieved by copolymerization of ProDOT-propargyl with dihexyl-substituted 3,4-propylenedioxythiophene, dihexyl-ProDOT.[12] The copolymerization of ProDOT-propargyl with dihexyl-ProDOT was studied with different amounts of dihexyl-ProDOT (ranging from 10% to 50%) using ferric chloride as an oxidant and chloroform as a solvent. It was found that the incorporation of 25% of the dihexyl-ProDOT resulted in the formation of a soluble copolymer (**P2**) with pendant "click"able terminal acetylenic units as side chains. This copolymer **P2** was purified by Soxhlet extraction, first with methanol to remove the monomer and oligomers and then with chloroform to get the pure polymer. Copolymer **P2** was found to be soluble in common organic solvents like chloroform, methylene chloride, tetrahydrofuran, and toluene and was characterized by NMR, FTIR, UV−vis spectroscopy, solution doping, and GPC. In order to study the changes in optical properties upon doping in case of **P2**, UV−vis spectra (Figure 2) were recorded in chloroform as a function of increasing concentration of the dopant (0.8 mM solution of $SbCl_5$ in chloroform). In the reduced state the copolymer **P2** shows a $\pi-\pi^*$ at 530 nm, and the intensity of this peak decreases with increase in the concentration of dopant. Furthermore, a new peak appeared upon the addition of the dopant at 944 nm which is due to the formation of polaron charge carriers upon doping. The intensity of the peak at 944 nm increases with an increase in concentration of the dopant. An isosbestic point was observed at 619 nm for the peaks at 530 and 944 nm, indicating that these two species are in equilibrium.

This soluble copolymer, **P2**, was then used for "click" chemistry by reacting it with carboxylic acid, ammonium, and alkyl azides to obtained polyanionic (**P2a**), polycationic (**P2b**), and neutral (**P2c**) polymers, respectively (Scheme 1). These polyelectrolytes were found to be soluble in water whereas the neutral **P2c** was soluble in organic solvents. These copolymers were characterized by FTIR and UV−vis spectroscopy, and the

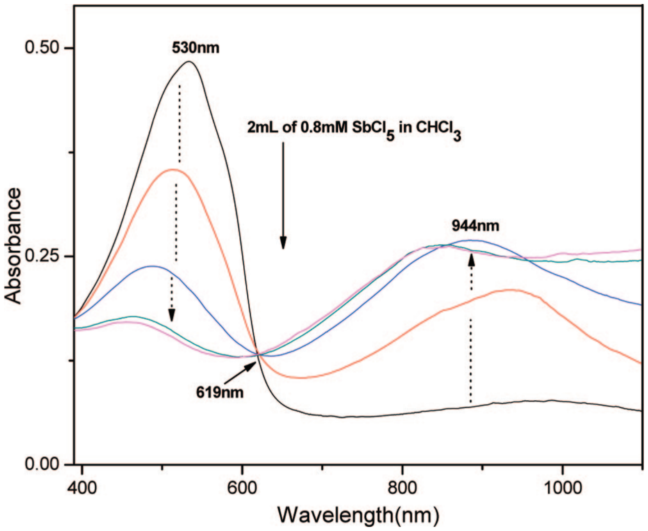


Figure 2. Solution doping of **P2** using 2 μL of 0.8 mM of $SbCl_5$ in $CHCl_3$ with an isosbestic point at 619 nm.

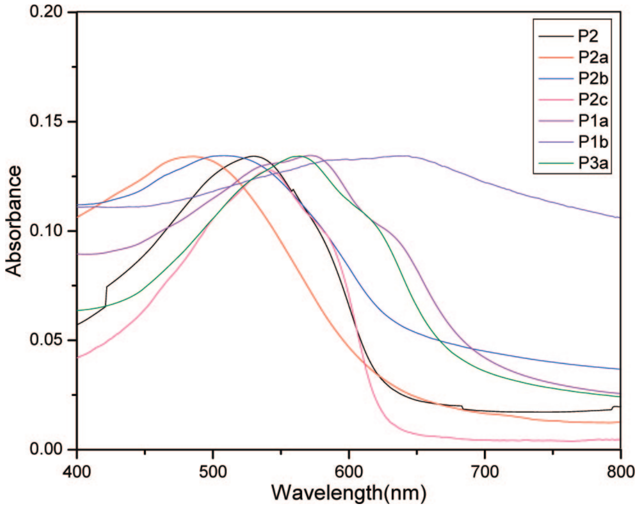


Figure 3. UV−vis absorbance spectra of **P1a** (purple), **P1b** (violet), **P2a** (red), **P2b** (blue), and **P3a** (green) in water and that of **P2** (black) and **P2c** (pink) in $CHCl_3$.

Table 1. Properties of Polymers

polymer	solubility	nature of side chain	M_w (PD)	λ_{max} (nm)	E (eV)
P1	insoluble	neutral			
P1a	H_2O	polyanionic	4900^b (1.44)	571, 629	1.84
P1b	H_2O	polycationic	4000^b (1.51)	582, 635	1.77
P2	$CHCl_3$, THF, toluene	neutral	5000^a (1.11)	530	2.00
P2a	H_2O	polyanionic	5700^b (1.41)	502	2.09
P2b	H_2O	polycationic	5650^b (1.42)	510	1.99
P2c	$CHCl_3$, THF, toluene	neutral	5200^a (1.45)	540	2.00
P3a	H_2O	polyanionic	4800^b (1.60)	562	1.82

[a] Determined by GPC relative to polystyrene standards. [b] Determined by GPC relative to polystyrenesulfonate standards.

average molecular weights were determined using GPC in appropriate solvents (Table 1). The FTIR spectra of the "click"ed polymer showed the absence of the acetylenic stretching frequency at 2329 cm^{-1}, indicating the success of "click" chemistry on the polymeric backbone. The success of "click" chemistry in case of **P2c** was further confirmed by ^1H NMR wherein a peak at 7.72 ppm was observed due to the triazole proton and the disappearance of the acetylenic protons at 2.4 ppm. The UV−vis spectra (Figure 3) of the neutral polymer **P2c** showed an absorption maxima at 540 nm typical of the $\pi-\pi^*$ transition in soluble 3,4-propylenedioxythiophene-based polymers. However, the polymeric nature of the resulting polymers was confirmed by UV−vis spectroscopy and GPC. The UV−vis spectra of the polyanionic (**P2a**) polymer showed an absorption maxima at 502 nm indicative of its polymeric nature whereas the polycationic polymer (**P2b**) showed an absorption maxima at 510 nm. GPC studies indicated a weight-average molecular weight of 5700 Da (PD of 1.41) for polyanionic **P2a**, 5650 Da (PD of 1.42) for polycationic **P2b**, and 5200 (PD of 1.45) for neutral **P2c**, further confirming the polymeric nature of the final product.

Monomers **Ma**−**Md** were also polymerized under oxidative conditions using ferric chloride as the oxidant in chloroform. In the case of monomers **Mc** and **Md**, the color of the solution changed from light yellow to green and finally to dark blue upon polymerization. The final polymers **P3c** and **P3d** were isolated by precipitating the polymerization mixture into methanol, followed by stirring it with hydrazine hydrate to undope the polymers. The undoped polymers were then washed with methanol and centrifuged to get dark blue powders and were found to be insoluble in common organic solvents. This was not surprising as the other reported polymers based on monosubstituted 3,4-propylenedioxythiophene were also found to be insoluble.[24] These insoluble polymers were characterized by FTIR spectroscopy. In case of monomers **Ma** and **Mb**, the polymerization was carried out in the solid state as these monomers were insoluble in chloroform. In the case of **Ma**, the carboxylic acid was converted in its sodium salt using 1 M sodium hydroxide solution. Removal of water under vacuum resulted in the formation of white solid which was further purified by washing with methanol to remove excess of sodium hydroxide. The resulted sodium salt was then used for polymerization using ferric chloride as oxidant and chloroform as the solvent. The polymerization proceeded in the usual fashion wherein color change from light yellow to light green to dark blue with time was observed. The final polymer **P3a** was isolated by precipitating the reaction mixture in methanol followed by stirring it with hydrazine hydrate to undope the polymer. Polymer **P3a** was finally washed with 1% methanolic solution of sodium hydroxide to convert counterions back to sodium. The resulting undoped polymer was isolated as a dark blue powder and was found to be insoluble in common organic solvents but was soluble in water. This polymer showed an absorption at λ_{max} 562 nm with a band gap of 1.82 eV. Polymer **P3a** was further characterized by FTIR spectroscopy. Surprisingly, all the attempts to polymerize monomer **Mb** using ferric chloride as an oxidant in chloroform were futile as no polymer was isolated. This is also in agreement with the observations made by Galand wherein she too was unsuccessful in polymerizing the ProDOT-based monomers with cationic side chain using various polymerization methods.[25] This further highlights the importance of "click" chemistry as an alternative route for the successful synthesis of conjugated polymer based on ProDOT with cationic side chain as demonstrated in this paper.

Electrochemical Studies. Chemical polymerization of ProDOT-propargyl resulted in an insoluble material, and hence electropolymerization was carried out in order to get a thin film of the final polymer for electrochemical studies. For electropolymerization, a platinum wire was used as the working electrode, a platinum foil as the counter electrode, and Ag/Ag^+ (0.01 M $AgNO_3$) as the reference electrode. Electrochemical polymerization of 0.02 M solution of ProDOT-propargyl in acetonitrile was carried out in presence of 0.1 M TBAP as the supporting electrolyte, using the potentiodynamic method by scanning the potential between −0.60 and +1.20 V (vs Ag/Ag^+). In the first forward scan, oxidation of the monomer was observed at +1.21

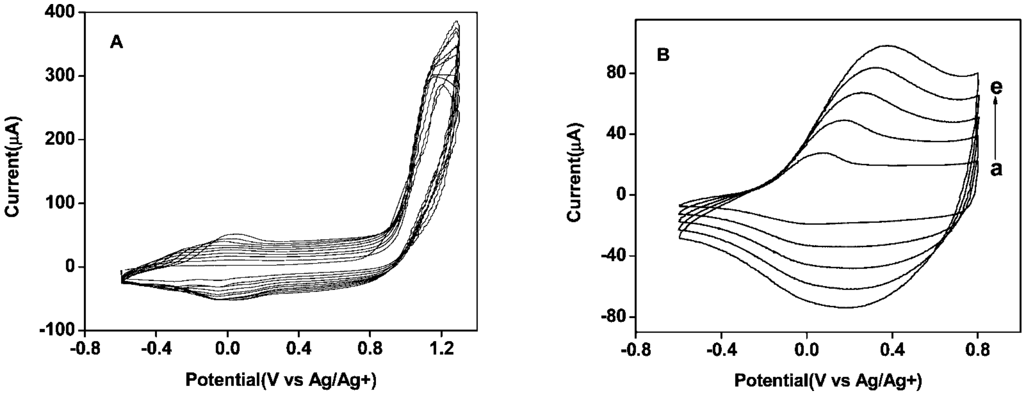


Figure 4. (A) Potentiodynamic growth of poly(ProDOT-propargyl) from 0.02 M in 0.1 M TBAP at the scan rate of 100 mV/s. (B) Scan rate dependence of poly(ProDOT-propargyl) in 0.1 M TBAP at the scan rate of (a) 50, (b) 100, (c) 150, (d) 200, and (e) 250 mV/s.

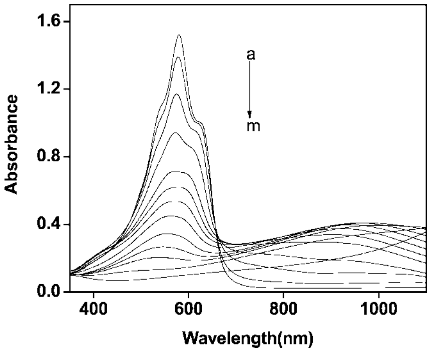


Figure 5. Optoelectrochemical spectra of the poly(ProDOT-propargyl) as a function of applied potential in 0.1 M TBAP/ACN where (a) −1, (b) −0.4, (c) −0.2, (d) −0.1, (e) −0.05, (f) 0.05, (g) 0.1, (h) 1.5, (I) 0.2, (j) 0.3, (k) 0.4, (l) 0.6, and (m) 1 V.

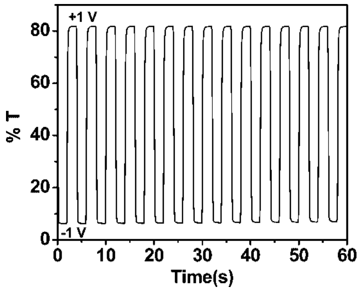


Figure 6. Optical switching studies for poly(ProDOT-propargyl) film monitored at 580 nm, when it was stepped between its reduced (−1.0 V) and oxidized (+1.0 V) state.

V (Figure 4A). In the subsequent cycles, polymer redox started appearing at a lower potential with a broad peak around +0.02 V during the anodic scan and a broad reduction peak at +0.014 V during the cathodic scan. In order to study the behavior of the polymer, cyclic voltammometric studies were carried out with the electrodeposited polymer in 0.1 M solution of TBAP in monomer-free acetonitrile by cycling the potential between −0.60 and +0.60 V at the scan rate of 50, 100, 150, 200, and 250 mV/s (Figure 4B). An oxidation peak was observed at +20 mV, and the corresponding reduction peak was observed at +14 mV. The polymer oxidation current increases linearly as a function of the scan rate, indicating that the surface-adsorbed polymer is electroactive.

Spectroelectrochemistry of the polymer was studied by using ITO-coated glass as the working electrode. The polymers were formed by electropolymerization of the monomer by applying a static potential of +1.20 V. This quickly resulted in the formation of a homogeneous films on the ITO electrode. The polymer film was then repeatedly washed with acetonitrile to remove the monomer and oligomers, and a series of UV−vis spectra of the polymer were then recorded in 0.1 M solution of TBAP in acetonitrile at different applied potentials using silver wire as a reference electrode and platinum foil as the counter electrode. The polymer was found to be opaque blue at −1 V and exhibited an absorption maxima at 580 nm which is assigned to the $\pi-\pi^*$ transition. Furthermore, two shoulders were also observed at 538 and 623 nm which arise due to the vibronic coupling, a phenomenon commonly observed in case of substituted ProDOT-based polymers (Figure 5).[13] Stepwise oxidation of the polymer showed a reduction in absorbance throughout the visible region as the color changes from the dark blue absorbing state (fully reduced form) to a highly transmissive state (oxidized form). The interesting feature to note in Figure 5 is the growth of the peak at 950 nm which is due to the polaron charge carriers. The intensity of this peak increases during the initial oxidation of the polymer but subsequently decreases in intensity upon further oxidation of the polymer. This result in a more color neutral appearance of the thin film as the near-infrared tail is eliminated, resulting in a higher contrast electrochromic material. This is attributed to the formation of bipolarons and is in agreement with the other reported polymers based on 3,4-propylenedioxythiophene derivatives.[13] The contrast calculated from the difference in %*T* between the completely reduced and oxidized state was found to be 75%. For optical switching studies, polymer films were synthesized on ITO-coated glass slides in the same manner as described above and were stepped between its reduced state (at −1.00 V) and oxidized state (at +1.00 V). While the film was switched, %*T* at 580 nm was monitored as a function of time (Figure 6). The switching of the film was carried out by switching the potential between −1.00 and +1.00 V with a delay time of 2 s while monitoring the %*T* of the polymer at its $\lambda_{\max}$(580 nm). The switching time of the polymer was calculated from 95% of its full contrast and was found to be around 500 ms.

In situ conductance measurements of poly(ProDOT-propargyl) were carried out using a gold-coated isoporous polycarbonate membrane with a pore diameter of 1.2 μm and thickness of 10 μm as the working electrode. A platinum foil and SCE was used as the counter and reference electrode, respectively. The polymers were synthesized by cycling the potential between −0.60 and +1.20 V at a scan rate of 100 mV/s. The polymers were grown on gold-coated membranes to bridge both sides of the membrane through the pores. In situ conductance of polymer poly(ProDOT-propargyl) was measured at various potentials starting from −0.60 and +0.90 V. At −0.60 V, i.e., in the reduced state, the polymer is an insulator and, hence, exhibits a low conductance. As the potential reaches +0.10 V, there is an increase in the conductance of the film (Figure 7). The conductance of the polymer continues to increase with the

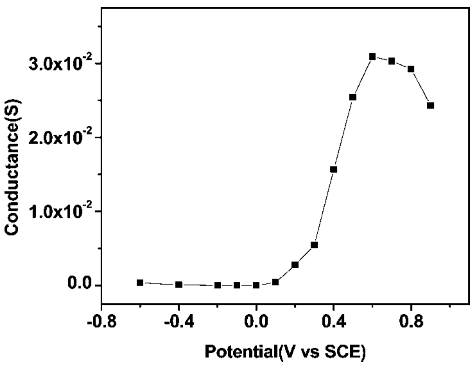


Figure 7. In situ conductance of poly(ProDOT-propargyl) in 0.1 M $KClO_4$ as a function of applied potential.

oxidation of the polymer and reaches its maximum conductance of 3.09×10^{-2} S at +0.60 V. The film shows a change in conductance of 3 orders of magnitude while going from insulating to conducting state.

In summary, we have shown, successfully, the synthesis and characterization of regioregular, processable, and "click"able monomer and polymers based on ProDOT. Though the homopolymer of ProDOT-propargyl was found to be insoluble in common solvents, it could be made water-soluble by performing "click" chemistry using suitable azides containing ionic groups. However, incorporation of 25% of the dihexyl-substituted 3,4-propylenedioxythiophene resulted in the syntheses of soluble and "click"able copolymers. We have clearly demonstrated the advantage of the present approach over the reported ones in terms of fine-tuning of the solubility of the final polymers, scalability due to chemical polymerization, and regioregular nature of the resulting polymers. This brings out new opportunities wherein monomers or conjugated polymers based on 3,4-propylenedioxythiophene with diverse functionalities can be easily synthesized in a single step starting from a single precursor, using "click" chemistry. In fact, this is the first time wherein a successful synthesis of polycationic conjugated polymer based on 3,4-propylenedioxythiophene is reported.

Experimental Section

Instrumentation and Methods. GPC was performed on 600 × 7.5 mm Polymer Laboratories PLgel 5 μm mixed D column for chloroform soluble polymers and using buffer solution (70% 0.2 M $NaNO_3$, 0.01 M NaH_2PO_4, pH 7, 30% MeOH) with two 300 × 7.5 mm Polymer Laboratories PL aquagel-OH 8 μm mixed column for water-soluble polymers with UV detector. Polymer solutions were prepared in chloroform and water, as per the solubility and filtered through a 0.45 μm filter before injection. A constant flow rate of 1 mL/min was used. Molecular weights were obtained relative to polystyrene standards for chloroform soluble polymer, whereas polystyrenesulfonate standards for water-soluble polymers. ^{1}H NMR and ^{13}C spectra were recorded on a Varian Mercury 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. UV absorption spectra were recorded with a Perkin-Elmer Lambda 35 UV/vis spectrophotometer, corrected for baseline with a solvent-filled cuvette. Infrared spectroscopy was performed on Perkin-Elmer Spectrum One FTIR-spectrometer using NaCl window. Electrochemical experiments were carried out in EG&G PAR model 362 potentiostat/galvanostat and a Pine Bipotentiostat AFCBP1 with Pine Chem 2.7.9 software. For optical switching studies EG&G PAR model 273 potentiostat/galvanostat was used to control the potential. Conductance of the polymers was measured in AFRDE4 PINE bipotentiostat coupled with a Philips 2525 multimeter. For electrochemical characterization a Pt wire was used as working electrode with Pt foil as counter electrode and Ag/Ag^+ as the reference electrode. ITO-coated glass slides were used as working electrode for spectroelectrochemical experiments.

Materials. Tetrahydrofuran was distilled over sodium benzophenon ketyl under nitrogen prior to use. Acetone and methylene chloride were used after distillation over calcium chloride. 3-Bromopropylamine hydrobromide and 2-(2-chloroethoxy)ethanol were purchased from Aldrich. Tetrabutylammonium perchlorate (TBAP) and lithium perchlorate ($LiClO_4$) were purchased from Fluka and was used without further purification. HPLC grade acetonitrile from Spectrochem was distilled over P_2O_5 and dried over CaH_2. All other chemicals were of reagent grade and used without further purification. Polycarbonate membrane was purchased from Millipore Corp. The membrane used was 10 μm thick with pore diameter of 1.2 μm. Indium-doped tin oxide (ITO)-coated glass slides were obtained from Delta Technologies.

1-Azidoethanoic Acid (a). To the solution of 1 g (7.1 mmol) of bromoacetic acid in 10 mL of acetone was added 1.1 g (16.9 mmol) of sodium azide. The mixture was kept for reflux at 80 °C for 48 h. The solvent was removed under reduced pressure. The residue was dissolved in 20 mL of methanol and recrystallized to obtain a white solid. Yield: 73%. ^{1}H NMR(CD_3OD, δ ppm): 3.66 (s). ^{13}C NMR (CD_3OD): 53.95, 168.7. IR (cm^{-1}): 3566, 2865, 2116, 1640.

(3-Azidopropyl)trimethylammonium Iodide (b). To the solution of 0.1 g (0.46 mmol) of 3-bromopropylamine hydrobromide in 5 mL of water was added 0.074 g (1.13 mmol) of sodium azide. The solution was kept for reflux at 80 °C for 15 h. The resulting solution was treated with 5%NaOH solution and then extracted with 20 mL of diethyl ether. The combined organic layer was dried over $NaSO_4$ and concentrated at reduced pressure to get yellow liquid. The pale yellow liquid hence obtained was dissolved in 10 mL of CH_2Cl_2 and added to it 5 mL of CH_3I, and the solution was stirred at room temperature for 6 h. The solvent was removed which resulted in a quaternized ammonium salt as yellow viscous liquid. Yield: 87%. ^{1}H NMR (D_2O, δ ppm): 1.92 (m, 2H), 3.07 (t, 2H, $J = 7.63$ Hz), 3.13 (s, 9H), 3.49 (t, 2H, $J = 6.41$ Hz). ^{13}C NMR (D_2O): 24.94, 50.85, 55.77, 66.64. IR (cm^{-1}): 3367, 2940, 2872, 2105, 1598, 1457, 1342, 1259, 1068.

1-Azidohexane (c). To the solution of 1.73 g (26.6 mmol) of sodium azide in 53 mL of DMSO was added 4 g (24.2 mmol) of 1-bromohexane. The solution was stirred at room temperature for 4 h. The resulting solution was then poured into 100 mL of water and extracted twice with 30 mL of diethyl ether. The combined organic layer was dried over $NaSO_4$ and concentrated at reduced pressure to get yellow liquid. Yield: 99%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.89 (t, 3H, $J = 6.72$ Hz), 1.2−1.6 (m, 8H), 3.25 (t, 2H, $J = 7.02$ Hz). ^{13}C NMR ($CDCl_3$): 13.82, 22.42, 26.31, 28.72, 31.25, 51.38. IR (cm^{-1}): 3327, 2959, 2930, 2861, 2095, 1466, 1378, 1264, 1119, 1027, 882, 728.

2-(2-Azidoethoxy)ethanol (d). To the solution of 2 g (0.016 mmol) of 2-(2-chloroethoxy)ethanol in 10 mL of water was added 2.6 g (40 mmol) of sodium azide. The solution was kept for reflux at 80 °C for 15 h. The resulting solution was treated with 5%NaOH solution and then extracted with 40 mL of diethyl ether. The combined organic layer was dried over Na_2SO_4 and concentrated at reduced pressure to get pale yellow viscous liquid. Yield: 80%. ^{1}H NMR ($CDCl_3$, δ ppm): 2.55 (s, 1H), 3.42(t, 2H, $J = 5.19$ Hz), 3.62 (t, 2H $J = 3.36$ Hz), 3.70 (t, 2H, $J = 4.88$ Hz), 3.76 (t, 2H, $J = 4.27$ Hz). ^{13}C NMR ($CDCl_3$): 50.62, 61.56, 69.87, 72.38. IR (cm^{-1}): 3400, 2929, 2872, 2524, 2106, 1644, 1444, 1346, 1286, 1127, 1066, 922, 880.

3-Methyl-3-prop-2-ynyloxymethyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepine (Pro-DOT-propargyl). To a suspension of 0.75 g (31.2 mmol) of NaH (60% in mineral oil) in 5 mL of anhydrous THF, a solution of 2.5 g (12.5 mmol) of Pro-DOT-OH in 5 mL of anhydrous THF was added dropwise under argon atmosphere. The resulting mixture was stirred for half an hour followed by the addition of DABCO (1 crystal) in catalytic amount. Then to the mixture 3.15 g (15 mmol) of propargyl tosylate was added dropwise. The mixture was stirred for 48 h under an argon atmosphere. The reaction mixture was poured then into 100 mL of water and extracted 3−4 times from 40 mL of ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to get a dark brown viscous oil. The crude product was then purified by silica gel column chromatography eluting with petroleum ether−ethyl acetate mixture to get pale yellow liquid. Yield: 50.4%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.99 (s, 3H), 2.44 (t, 1H, $J = 2.4$ Hz), 3.59 (s, 2H), 3.72 (d, 2H, $J = 11.9$ Hz), 4.02 (d, 2H, $J = 11.9$ Hz), 4.17 (dd, 2H, $J = 2.4$ Hz), 6.48 (s, 2H). ^{13}C NMR ($CDCl_3$): 17.45, 43.26, 58.89, 72.64, 74.71, 76.70, 105.71, 149.89. IR (cm^{-1}): 32.88, 2962, 28.56, 2117, 1634, 1568, 1486, 1450, 1328, 1267, 1226, 1186, 1134, 1098, 1032, 849, 784, 729, 626. HRMS: calcd for $C_{12}H_{14}O_3S$ $(M + H)^+$, 239.0742; found: 239.0737.

[4-(3-Methyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepin-3-ylmethoxymethyl)-1,2,3-triazol-1-yl]acetic Acid (Ma). To the solution of 0.05 g (0.21 mmol) of Pro-DOT-propargyl in 1 mL of DMSO was added 0.021 g (0.21 mmol) of 1-azidoethanoic acid. To the resulting solution, a solution of 0.029 g (0.15 mmol) of sodium ascorbate in 0.3 mL of water and a solution of 0.01 g (0.042 mmol) of $CuSO_4$ in 0.1 mL of water were added. The mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure. To the residue 10 mL of water was added and extracted twice from 20 mL of chloroform. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield a white solid. Yield: 93%; mp 97 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.91 (s, 3H), 3.56 (s, 2H), 3.65 (d, 2H, $J = 11.9$ Hz), 3.97 (d, 2H, $J = 11.9$ Hz), 4.65 (s, 2H), 5.15 (s, 2H), 6.45 (s, 2H), 7.72 (s, 1H). ^{13}C NMR ($CDCl_3$): 17.23, 43.28, 50.88, 64.64, 73.08, 76.32, 105.73, 124.25, 145.28, 149.74, 168.19. IR (cm^{-1}): 3433, 1645, 1485, 1188, 1023, 953, 778. HRMS: calcd for $C_{14}H_{17}N_3O_5S$ $(M + H)^+$, 340.0967; found: 340.0962.

Trimethyl-{3-[4-(3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepin-3-ylmethoxymethyl)-1,2,3-triazol-1-yl]propyl}ammonium Iodide (Mb). To the solution of 0.05 g (0.21 mmol) of Pro-DOT-propargyl in 1 mL of acetone was added 0.056 g (0.21 mmol) of (3-azidopropyl)trimethylammonium iodide. To the resulting solution, a solution of 0.029 g (0.15 mmol) of sodium ascorbate in 0.3 mL of water and a solution of 0.01 g (0.042 mmol) of $CuSO_4$ in 0.1 mL of water were added. The mixture was stirred at 80 °C for 96 h. The solvent was removed under reduced pressure. To the residue 10 mL of chloroform was added. The chloroform layer was transferred and evaporated to get yellow liquid. Yield: 87%. ^{1}H NMR (D_2O, δ ppm): 0.97 (s, 3H), 1.99 (m, 2H), 3.01 (s, 9H), 3.36 (t, 2H, $J = 7.63$ Hz), 3.5 (s, 2H), 3.62 (d, 2H, $J = 11.9$ Hz), 3.88 (d, 2H, $J = 11.9$ Hz), 4.42 (t, 2H, $J = 3.33$ Hz), 4.72 (s, 2H), 6.47 (s, 2H), 7.89(s, 1H). ^{13}C NMR (D_2O): 17.23, 26.60, 43.26, 46.67, 47.51, 54.11, 64.84, 72.83, 76.65, 105.91, 123.69, 145.08, 149.80. IR (cm^{-1}): 3434, 2969, 1774, 1620, 1486, 1381, 1218, 1187, 1095, 1025, 759. HRMS: calcd for $C_{18}H_{29}N_4IO_3S$ $(M - I)^+$, 381.1960; found: 381.1968.

1-Hexyl-4-(3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepin-3-ylmethoxymethyl)-1*H*-1,2,3-triazole (Mc). To the solution of 0.05 g (0.21 mmol) of Pro-DOT-propargyl in 1 mL of acetone was added 0.026 g (0.21 mmol) of 1-azidohexane. To the resulting solution, a solution of 0.029 g (0.15 mmol) of sodium ascorbate in 0.3 mL of water and a solution of 0.01 g (0.042 mmol) of $CuSO_4$ in 0.1 mL of water were added. The mixture was stirred at 80 °C for 96 h. The solvent was removed under reduced pressure. To the residue 10 mL of water was added and extracted 3−4 times from 10 mL of ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield brown viscous liquid. The crude product was then purified by silica gel column chromatography eluting with petroleum ether, ethyl acetate mixture (80:20) to get pale yellow liquid. Yield: 81.3%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.87 (t, 3H, $J = 6.96$ Hz), 0.96 (s, 3H), 1.2−1.9 (m, 8H), 3.57 (s, 2H), 3.67 (d, 2H, $J = 11.91$ Hz,) 3.8 (d, 2H, $J = 11.91$ Hz), 4.34 (t, 2H, $J = 7.33$ Hz), 4.67 (s, 2H), 6.46 (s, 2H), 7.51 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.84, 17.33, 22.34, 26.09, 30.18, 31.07, 43.30, 50.31, 65.21, 72.95, 76.65, 105.53, 121.97, 145.18, 149.83. IR (cm^{-1}): 2961, 2927, 2856, 1486, 1454, 1380, 1260, 1216, 1023, 799, 761. HRMS: calcd for $C_{18}H_{27}N_3O_3S$ $(M + H)^+$, 366.1851; found: 366.1844.

2-{2-[4-(3-Methyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-1,4-dioxepin-3-ylmethoxymethyl)-1,2,3-triazol-1-yl]ethoxy}ethanol (Md). To the solution of 0.12 g (0.51 mmol) of Pro-DOT-propargyl in 1 mL of acetone was added 0.066 g (0.51 mmol) of 2-(2-azidoethoxy)ethanol. To the resulting solution, a solution of 0.069 g (0.35 mmol) of sodium ascorbate in 0.3 mL of water and a solution of 0.026 g (0.11 mmol) of $CuSO_4$ in 0.1 mL of water were added. The mixture was stirred at 80 °C for 96 h. The solvent was removed under reduced pressure. To the residue 10 mL of water was added and extracted 3−4 times from 10 mL of ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield a brown viscous liquid. Yield: 85.5%. ^{1}H NMR (CD_3OD, δ ppm): 0.96 (s, 3H), 1.96 (s, 1H), 3.51 (t, 2H, $J = 5.19$ Hz), 3.56 (s, 2H), 3.63 (t, 2H, $J = 3.16$ Hz), 3.66 (d, 2H, $J = 11.91$ Hz), 3.87 (t, 2H, $J = 5.13$ Hz), 3.98 (d, 2H, $J = 11.91$ Hz), 4.58 (t, 2H, $J = 5.13$ Hz), 4.61 (s, 2H), 6.47 (s, 2H), 7.71(s, 1H). ^{13}C NMR (CD_3OD): 17.54, 30.55, 61.47, 64.98, 69.21, 72.44, 76.59, 105.54, 123.44, 145.22, 149.73. IR (cm^{-1}): 3418, 2973, 1704, 1486, 1366, 1303, 1218, 1185, 1129, 1064, 1025, 951, 914, 849, 810. HRMS: calcd for $C_{16}H_{23}N_3O_5S$ $(M + H)^+$, 370.1437; found: 370.1440.

General Method for the Oxidative Polymerization of ProDOT-propargyl and Ma-d (P1, P3a−d). To the solution of 0.21 mmol of monomer in 20 mL of chloroform was added 0.94 mmol of anhydrous $FeCl_3$. The mixture was stirred for 72 h under an argon atmosphere. To the reaction mixture 1 mL of hydrazine hydrate was added and stirred for 5 h. After treating it with hydrazine hydrate, the reaction mixture was poured into 100 mL of methanol and precipitated out. The precipitate was obtained by centrifuging and was then vacuum-dried to get the final polymers as dark blue solid.

P1: Yield: 91%. IR (cm^{-1}): 2971, 2326, 1633, 1485, 1450, 1378, 1186, 1098, 1031, 778.

P3a: Yield: 81%. IR (cm^{-1}): 2969, 1652, 1480, 1182, 1022, 950.

P3c: Yield: 69%. IR (cm^{-1}): 2960, 2850, 1488, 1455, 1379, 1266, 1010.

P3d: Yield: 73%. IR (cm^{-1}): 2971, 1710, 1476, 1356, 1310, 1212, 1180, 1127, 1066, 1022, 949.

“Click” Chemistry with Poly(ProDOT-propargyl) Using Azidoacetic Acid (P1a). To a suspension of 0.01 g (0.04 mmol) of poly(ProDOT-propargyl) in 10 mL of DMSO was added 0.1 g (0.98 mmol) of azidoacetic acid. To the resulting mixture, a solution of 0.058 g (0.29 mmol) of sodium ascorbate in 1.5 mL of water and a solution of 0.024 g (0.096 mmol) of $CuSO_4$ in 1 mL of water were added. Then to the mixture 2 mL of 1 M NaOH solution in water was added. The mixture was stirred for 5 days. On removing DMSO/water from the reaction mixture a blue solid was obtained, and the solid was found to be soluble in water. Yield: 88%. IR (cm^{-1}): 3439, 2928, 1637, 1443, 1327, 1149, 875.

“Click” Chemistry with Poly(ProDOT-propargyl) Using (3-Azidopropyl)trimethylammonium Iodide (P1b). To a suspension of 0.01 g (0.04 mmol) of poly(ProDOT-propargyl) in 10 mL of DMSO was added 0.1 g (0.37 mmol) of (3-azidopropyl)trimethylammonium iodide. To the resulting mixture, a solution of 0.058 g (0.29 mmol) of sodium ascorbate in 1.5 mL of water and a solution of 0.024 g (0.096 mmol) of $CuSO_4$ in 1 mL of water were added. The mixture was stirred for 5 days. On removing DMSO/water from the reaction mixture a blue solid was obtained, and the solid was found to be soluble in water. Yield: 91%. ^{1}H NMR (DMSO-d_6, δ ppm): 1.16 (br, 3H), 1.76 (br, 2H), 8.1 (br, 1H). IR (cm^{-1}): 2924, 1650, 1447, 1327, 1149, 875.

Copolymerization of ProDOT-propargyl and Dihexyl-ProDOT (P2). To the solution of 0.09 g (0.21 mmol) of ProDOT-propargyl and 0.068 g (0.21 mmol) of Dihexyl ProDOT in 20 mL of chloroform was added 0.15 g (0.94 mmol) of anhydrous $FeCl_3$. The mixture was stirred for 72 h under an argon atmosphere. To the reaction mixture 1 mL of hydrazine hydrate was added and stirred for 5 h. After treating it with hydrazine hydrate, the reaction mixture was poured into 100 mL of methanol and precipitated out. The precipitate was then washed with methanol several times and centrifuged to obtain the purple solid. The purple solid was then subjected to Soxhlet apparatus for fractionation. 100 mL of methanol was refluxed over cotton for 5 h to remove the monomer and excess of ferric chloride. Finally 100 mL of chloroform was refluxed over cotton to get the pure polymer. The solvent was evaporated under reduced pressure, and the concentrated solution was poured into methanol for precipitating out. The precipitate was then vacuum-dried to obtain purple solid. The purple solid hence obtained was found to be soluble in chloroform. Yield: 55%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.89 (br, 6H), 1.25 (br, 3H), 1.57 (br, 20H), 2.48 (br, 1H), 3.52 (br, 2H), 3.73 (br, 2H), 3.97 (br, 4H), 4.21 (br, 4H). IR (cm^{-1}): 2917, 2329, 1731, 1657, 1462, 1371, 1259, 1045, 803.

General Procedure for "Click" Chemistry with P2. To a solution of (0.035 mmol) **P2** in acetone was added (0.11 mmol) azide in 0.5 mL of acetone. To the resulting solution, a solution of (0.021 mmol) sodium ascorbate in 0.3 mL of water and a solution of (0.011 mmol) $CuSO_4$ in 0.1 mL of water were added. The mixture was stirred at 80 °C for 96 h. Acetone was removed, and the resulting mixture was subjected to chloroform treatment or to methanol.

P2a: Yield: 79%. IR (cm^{-1}): 3434, 2923, 1607, 1440, 1294,1262, 1042.

P2b: Yield: 66%. IR (cm^{-1}): 2920, 1654, 1539, 1423, 1361, 1276, 1099, 821.

P2c: Yield: 73%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.87 (br, 3H), 1.02−1.62 (br, 29H), 2.02−2.38 (br, 6H), 3.61 (br, 4H), 3.85 (br, 4H), 4.22 (br, 6H), 7.81 (br, 1H). IR (cm^{-1}): 2923, 1742, 1462, 1377, 1361, 1256, 1080, 1017, 801.

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Supporting Information Available: ^{1}H NMR spectra of monomers **Mb**, **Mc**, and **Md** and polymers **P1b**, **P2**, and **P2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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