Supporting Information for:

Broadening Absorption in Conductive Polymers through Crosslinkable Side Chains in Non-conjugated Polymer Backbone

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Experimental Section:

$^1$H-NMR spectra were recorded on a 400 MHz NMR spectrometer using the residual proton resonance of the solvent as an 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. $^{13}$C-NMR spectra were proton decoupled and recorded on a 100 MHz NMR spectrometer using the carbon signal of deuterated solvent as an internal standard. UV-Visible spectra were obtained using a Cary 100 spectrophotometer. The molecular weights of the polymer were determined by size exclusion chromatography on a single injector mode GPC, using THF as an eluent and toluene as an internal reference; PMMA standard was used for calibration and output was received and analyzed using an RI detector. Flash chromatography was performed with 37-75 µm silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by a UV lamp. THF and toluene were distilled over Na/Ph$_2$CO ketyl. 3$^{rd}$ generation Grubbs catalyst$^1$, 3,4-propylenedioxythiophene derivative (ProDOT)$^{2,3}$ (3), 2-tributyl tin EDOT$^4,5$ (5) and 2-phenyl EDOT$^6$ (8) have been synthesized according to reported procedures. All other chemicals were obtained from commercial sources and used without any purification unless otherwise stated.

**Synthesis of 2,5-dibromoProDOT (3)**

![Chemical Structure](image)

In a two-necked 250 mL round-bottom flask filled with 20 mL chloroform, 0.60 g (3.00 mmol) of ProDOT (3) was added and the solution was bubbled under argon for 20 mins. Then, 1.11 g (9.00 mmol) of N-bromosuccinimide (NBS) was added and the mixture was stirred for 20 hours. 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 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)**

![Image 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 hours. After completion of the reaction, water was added and the mixture was extracted using CH$_2$Cl$_2$ (3x20 mL). Organic layers were collected and dried over anhydrous MgSO$_4$. The resulting residue was purified by column chromatography using 50% ethylacetate 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)**

![Image of diphenyl triADOT derivative (9)]

2-phenyl-5-tributyl tin EDOT (10) was prepared according to the following procedure. 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 hour 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 as an oily liquid which was further
used as a Stille reagent in the next step without further purification. \(^1\)H NMR (CDCl\(_3\), \(\delta\), 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\(_3\), \(\delta\), 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\(_3\))\(_2\)Cl\(_2\) was added and the mixture was stirred at 80 °C for 2 hours. After completion of the reaction, water was added and the mixture was extracted using CH\(_2\)Cl\(_2\) (3x20 mL). Organic layers were collected and dried over anhydrous MgSO\(_4\). The resulting residue was purified by column chromatography using 10% ethylacetate in dichloromethane. The product was obtained as a yellow solid with 17% yield. \(^1\)H NMR (CDCl\(_3\), \(\delta\), 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\(_3\))\(_2\)CO, \(\delta\), 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)**

![Image of 5-norbornene-exo-2-triADOT carboxylate (1)](image)

0.1 g (0.21 mmol) of triADOT (6) and 0.06 g (0.43 mmol) of 5-exo-norbornene-2-acetic acid (7) were dissolved in dry THF and the mixture was cooled down to 0°C. 0.09 g (0.43 mmol) of dicyclohexyl carbodiimide (DCC) followed by 0.05 g (0.43 mmol) of 4-dimethyl aminopyridine (DMAP) were added to the mixture one after other. The mixture was stirred at 0°C for 2 hour. After completion of the reaction, the precipitated dicyclohexyl urea was filtered. Then, water was added and the mixture was extracted using CH\(_2\)Cl\(_2\) (3x20 mL). Organic layers were collected and dried over anhydrous MgSO\(_4\). The resulting residue was purified by column chromatography using 30% ethylacetate in hexanes. The product was obtained as a yellow solid with 65% yield. \(^1\)H NMR (CDCl\(_3\), \(\delta\), 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\(_3\), \(\delta\), ppm): 176.2, 143.8, 141.0, 137.9, 137.2,
135.2, 113.1, 97.6, 66.3, 64.9, 46.6, 43.1, 41.4, 33.9, 30.4, 16.6. CI m/z [M]+ calcd for C_{29}H_{28}O_{8}S_{3}, 600.7, found 600.1.

**Synthesis of 5-norbornene-exo-2-diphenyl triADOT carboxylate (2)**

![Chemical Structure](image)

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-exo-norbornene-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% ethylacetate in hexanes. The product was obtained as a yellow solid with 69% yield. ^1H NMR (CDCl₃, 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). ^13C-NMR (CDCl₃, 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 CI m/z [M]^+ calcd for C_{41}H_{36}O_{8}S_{3}, 752.9, found 752.2.

**Copolymerization of monomers 1 and 2 using ROMP**

![Chemical Structure](image)

Dry THF was taken into a round bottom flask and was freeze-pumped-thawn 3 times before used. The mixture of 1:0, 0:1, 3:1, 1:1 and 1:3 ratios of monomers 1 and 2 and 3rd generation Grubbs catalyst were put under vacuum into two separated round bottom flasks for 30 mins 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 minutes 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 \textit{in vacuo} to yield polymers as yellow solid. \(^1\)H NMR (CDCl\textsubscript{3}, ppm) \(\delta\) 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).

**DSC and TGA of P1 and P2**

The thermal stability of P1 and P2 has been determined using DSC and TGA. Figure S1 and S2 shows DSC and TGA curves of P1 and P2, respectively.

**Figure S1** TGA (left) and DSC (right) curves of P1

**Figure S2** TGA (left) and DSC (right) curves of P2

**Cross-linked ROMP homopolymer of polynorbornene containing triADOT and diphenyl triADOT side chains by oxidative electropolymerization**

5.00 mg of polymers P1 and P2 in 1.00 mL dichloromethane were spun-coat onto ITO-coated glass at a rate of 1000 rpm. Electropolymerization was performed by scanning the potential between -800 mV and 800 mV using 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAPF\textsubscript{6}) as supporting electrolyte in acetonitrile. The scan rate was 100 mV/s.
Chemical cross-linking of P1-P5 using FeCl₃ followed by hydrazine

5.00 mg of polymers in 1.00 mL dichloromethane were spun-coat on a glass slide at a rate of 1000 rpm. The cross-linking of ROMP polymers were performed by dipping the film into an acetonitrile solution containing 0.01 M FeCl₃ 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 UV-Vis spectra.

Spectroelectrochemistry of M2

To substantiate that the peak appeared at around 500-700 nm observed in polymers after oxidation is attributed to the radical cation formation, we performed electrochemical studies of the monomer. In this study, 2.00 mg of M2 in 1.00 mL dichloromethane was dropped cast on an ITO coated glass. The electrochemical oxidation of the monomer film was performed at the potential between -200 mV and 1100 mV using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte in acetonitrile at the scan rate of 100 mV/s. The spectroelectrochemistry of M2 before and after oxidation is shown in figure S3. In neutral state, the monomer has an absorption signal at 350-500 nm, similar to the corresponding polymer. Upon oxidation, the signal at 500-700 nm appears as with the polymer thin film. However, note that the intensity of the peak in this thin film is weak. This is attributed to the fact that the monomer M2 does not form a good film on the ITO coated glass and the radical cation seems to be soluble in the electrolyte used in the study. However, the fact that the oxidized peak appears in the same region as the polymer strongly suggests that this is indeed due to the radical cation of the polymer.

![Absorption spectra of neutral (left) and oxidized (right) M2](image)

**Figure S3** Absorption spectra of neutral (left) and oxidized (right) M2

Oxidation of M1 and M2 in solution

To investigate whether there is a difference in the oxidation behavior of both crosslinkable and non-crosslinkable species in the solution and in the film, we chemically oxidized M1 and M2 in solution and their absorption spectra were monitored.

The absorption spectra of M1, M2 and their corresponding oxidized moieties are shown in Figure S4. Both monomers have an absorption at 350-400 nm similar to what we observed in a P1 and P2. In M1, after oxidation by FeCl₃ for 5 mins, there are 2 new absorption band appears at around 350-480 nm and at 600-800 nm. These absorption peaks are likely due to the radical cation and dication of M1, respectively. The broad
signal at 600-800 nm appears slightly blue shifted compared to what is observed in polymer case. This suggests that oxidation of M1 in solution might only lead to the formation of the oligomers, rather than polymers.

In M2, 2 new signals at 350-400 nm and 500-700 nm are also observed upon oxidation with FeCl₃. These are likely due to the radical cation and dication of the monomer M2. Interestingly, the broad signal at 500-700 nm is also observed earlier in P2. This supports our hypothesis that when alpha position of EDOT is blocked, polymerization is prohibited.

**Figure S4** Absorption spectra of M1, M2 and their oxidized corresponding counterparts.

References