Electronic Supporting Information *For*

Effect of Monomers' Structure on Self Acid Assisted-

Polycondensation for the Synthesis of Poly(3,4-

ethylenedioxythiophene) and Homopolythiophene

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1. ¹H-NMR and ¹³C-NMR spectra of the compounds

Figure S1. ¹H NMR (CDCl₃) spectrum of 7-Bromo-2,3,2',3'-tetrahydro-[5,5']bi[thieno[3,4-b][1,4]dioxinyl] (E-E-Br, 1)



Figure S2. ¹³C NMR (d-DMSO) spectrum of 7-Bromo-2,3,2',3'-tetrahydro-[5,5']bi[thieno[3,4-b][1,4]dioxinyl] (E-E-Br, 1)



Figure S3. ¹H NMR (CDCl₃) spectrum of 5-(5-Bromo-thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (E-S-Br, 4)



Figure S4. ¹³C NMR (CDCl₃) spectrum of 5-(5-Bromo-thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (E-S-Br, 4)



Figure S5. ¹H NMR (CDCl₃) spectrum of 2-(4-Hexyloxy-thiophen-2-yl)-4,4,5,5tetramethyl-[1,3,2]dioxaborolane (5)



Figure S6. ¹H NMR (CDCl₃) spectrum of 4-Hexyloxy-[2,2']bithiophenyl (6, S-S-OC₆)







Figure S8. ¹H NMR (CDCl₃) spectrum of 5-Bromo-4-hexyloxy-[2,2']bithiophenyl (S-S-OC₆-Br, 7)



Figure S9. ¹³C NMR (d-DMSO) 5-Bromo-4-hexyloxy-[2,2']bithiophenyl (S-S-OC₆-Br, 7)



Figure S10. ¹H-NMR spectra of the P(S-S-OHexy).



2. Figure S11. Typical GPC profiles of P(S-S-OHexy) obtained under different temperature.



3. Figure S12. Electrochemical impedance spectra of PEDOT-Br and PEDOT-I



EIS spectra were taken at a frequency range of 0.1 to 10^{5} Hz at 0 V DC potential with the amplitude of 5 mV. It was performed in a symmetrical two FTO electrode cells. A 0.1 M Bu₄ClO₄ actonitrole solution served as the electrolyte and sample thickness (0.3mg/cm⁻²) were kept almost the same.

4. Table S1 Electrochemical properties of the polymers

Polymer	E _{ox} ^a	$E_{red}{}^{a}$	HOMO/LUMO ^b (eV)	Band gap (eV)
P(E-S)	0.03	-1.53	-4.83/-3.27	1.56
P(S-S-Ohexy)	0.95	-0.48	-5.75/-4.32	1.43

a. Oxidation potentials of dyes in CH₃CN containing 0.1 M Bu₄NClO₄. (Vs Ag/AgCl) with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 630 mV; b. HOMO and LUMO calculated by E_{HOMO} =-(E_{ox} + 4.8- $E_{Fc/Fc}$ ⁺) eV, E_{LUMO} = -(E_{red} + 4.8- $E_{Fc/Fc}$ ⁺) eV.