Supporting Information

Enhanced and Unconventional Responses in Chemiresistive Sensors for Ammonia and Nitrogen Dioxide from Carboxylated Alkylthiophene Polymers

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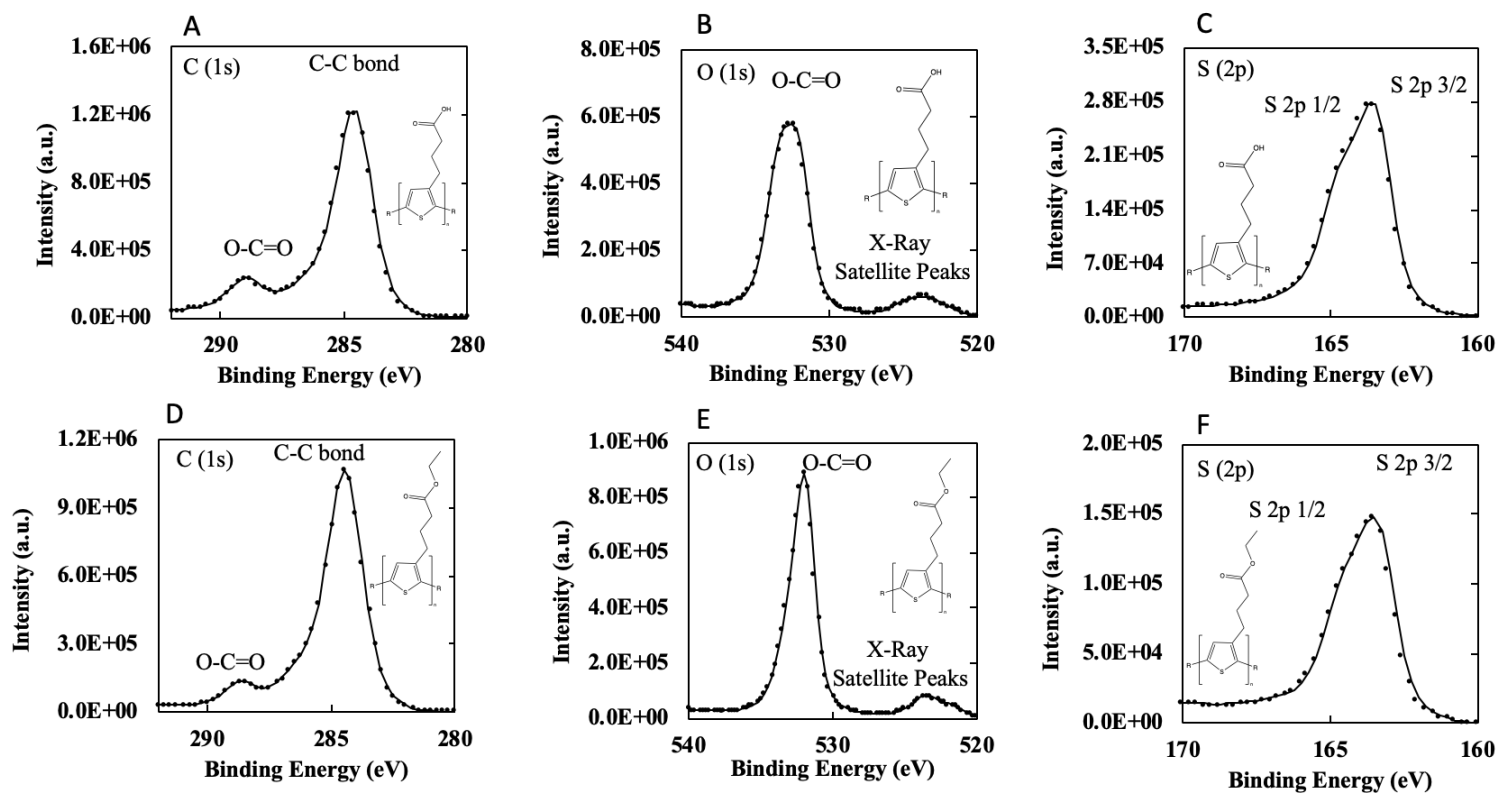# X-Ray Photoelectron Spectroscopy (XPS)

Figure S1. Core level spectra of C 1s, S 2p, and O 1s for A,B,C) PT-COOH and D, E,F) PT-COOR thin film on Si/SiO_2 (300 nm).
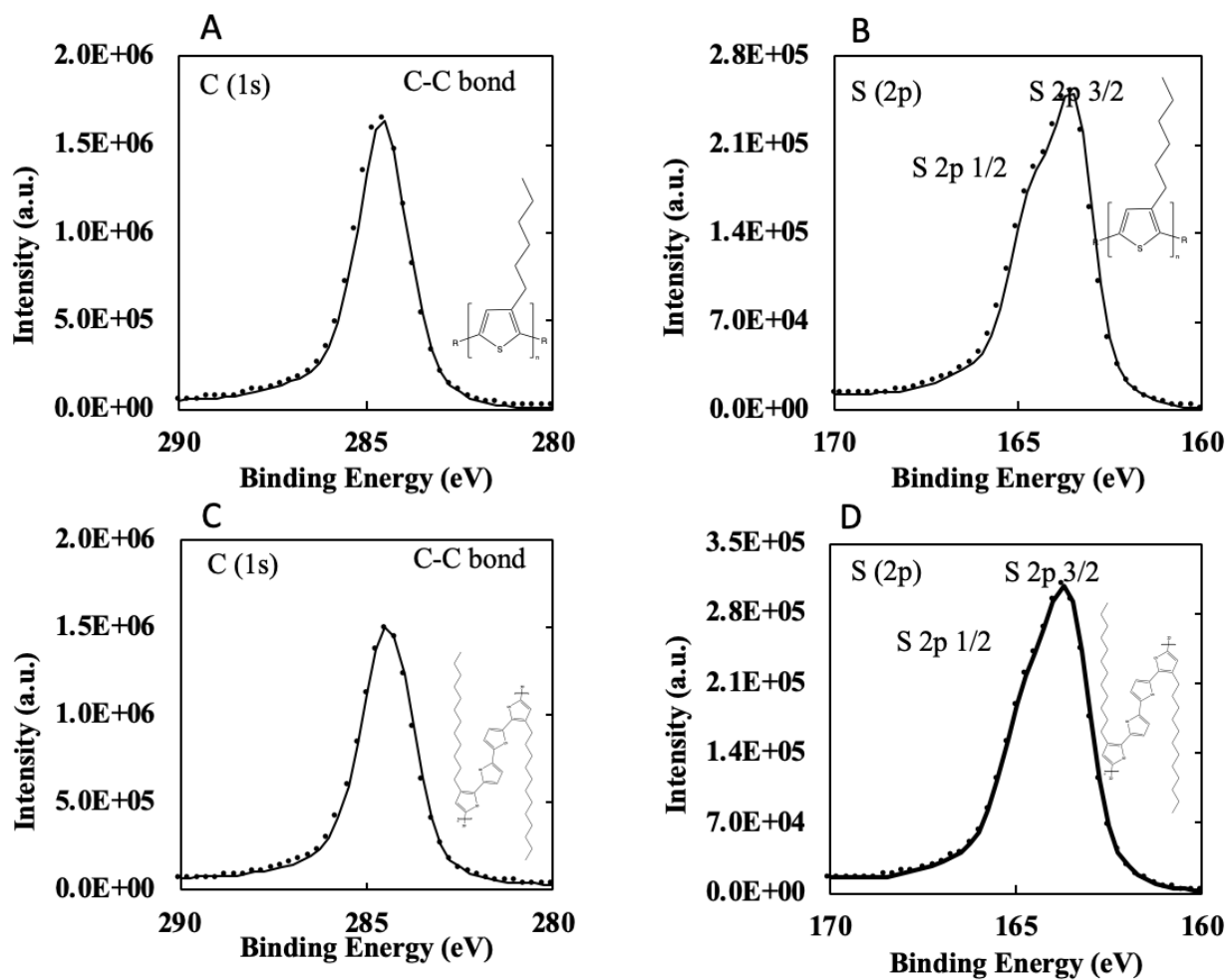
Figure S2. Core level spectra of C 1s and S 2p, for A,B) P3HT and C,D) PQT12 thin film on Si/SiO$_2$ (300 nm).
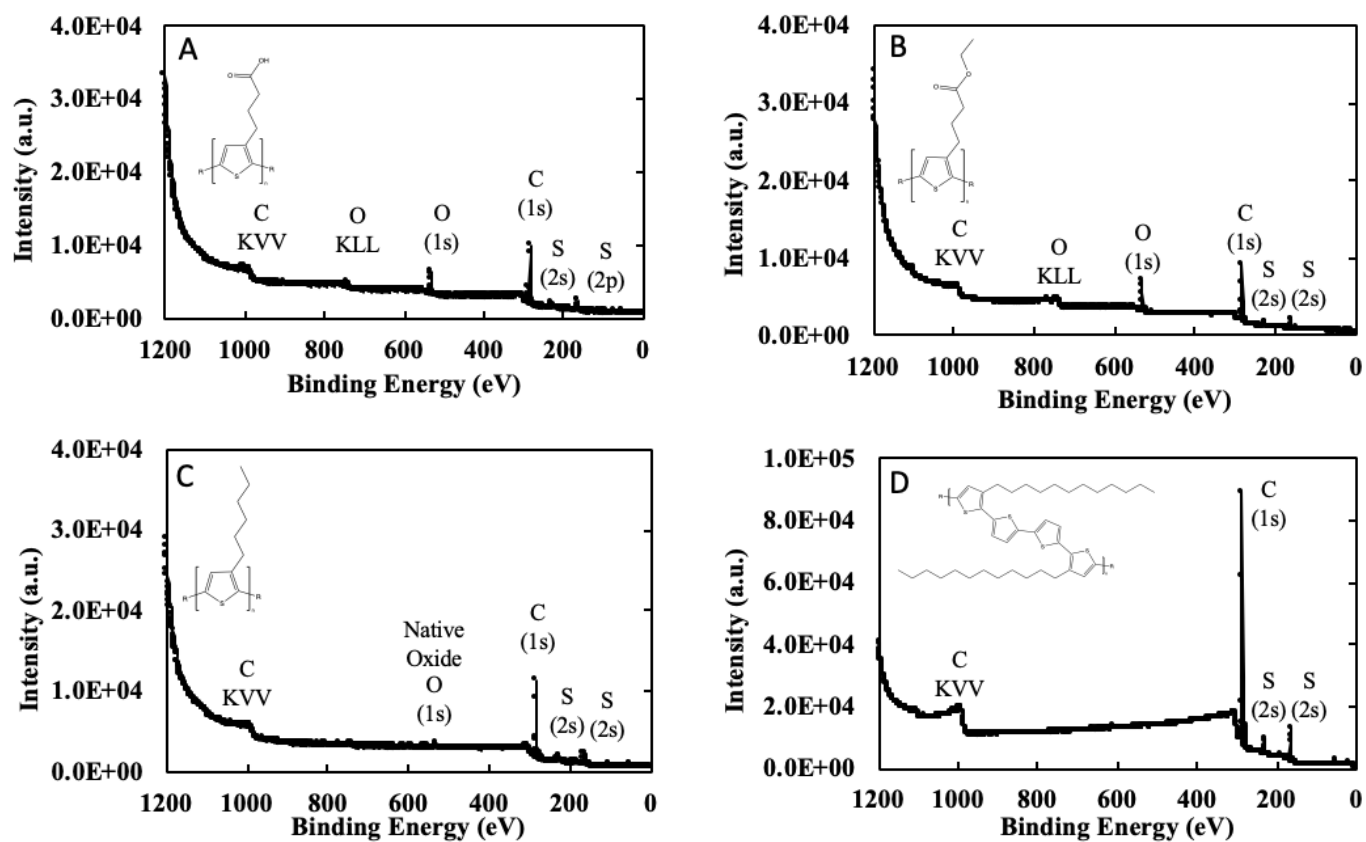
Figure S3. Full surface scan of A) PT-COOH, B) PT-COOR, C) P3HT, D) PQT12 thin film on Si/SiO₂ (300 nm) surface compositional analysis using XPS.

Polymer Sensing Layer	Film Thickness (nm)	V_T (V)	I_{on}/I_{off}	μ (cm^2/ V•s)
P3HT	20 ± 5	8-13	310	$1.8 \times 10^{-4} \pm 7E\text{-}5$
PQT12	20 ± 5	-18.5	340	$5.4 \times 10^{-4} \pm 2E\text{-}4$
PT-COOR	20 ± 5	3-14	1.1	$1.2 \times 10^{-2} \pm 6E\text{-}3$
PT-COOH	20 ± 5	14-18	1.1	$2.3 \times 10^{-2} \pm 8E\text{-}3$

Table S1. Transistor characteristic parameters of OFET configured flexible devices for PT-COOH, PT-COOR, P3HT, and PQT12.

Figure S4. Theoretical Extraction of LOD for each polymer sensing layer A) PT-COOH, B) PT-COOR, C) P3HT, D) PQT12 with exposure to various concentrations of NO$_2$ for 3 minutes before each consecutive measurement under continuous flow analysis. Slope represents sensitivity response % per ppm.
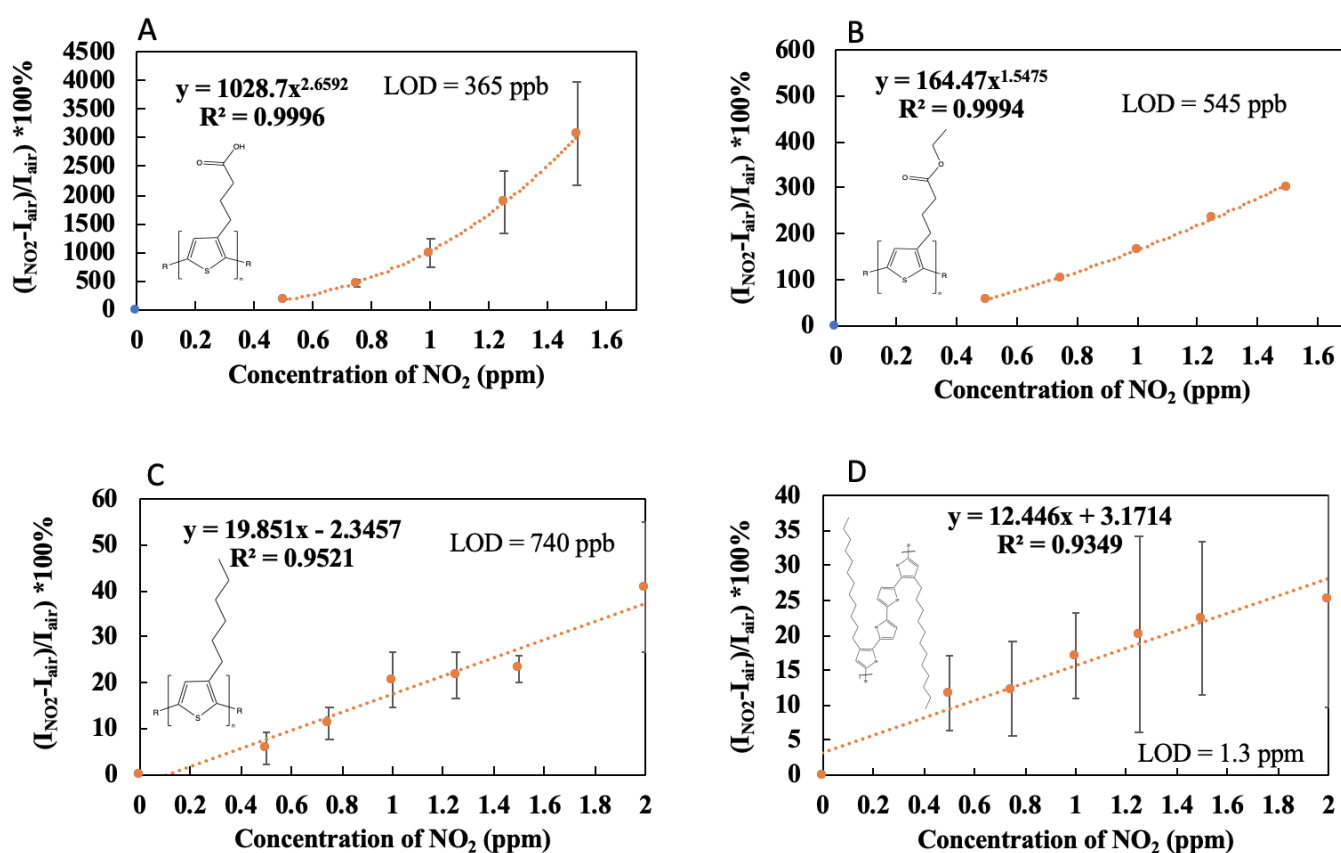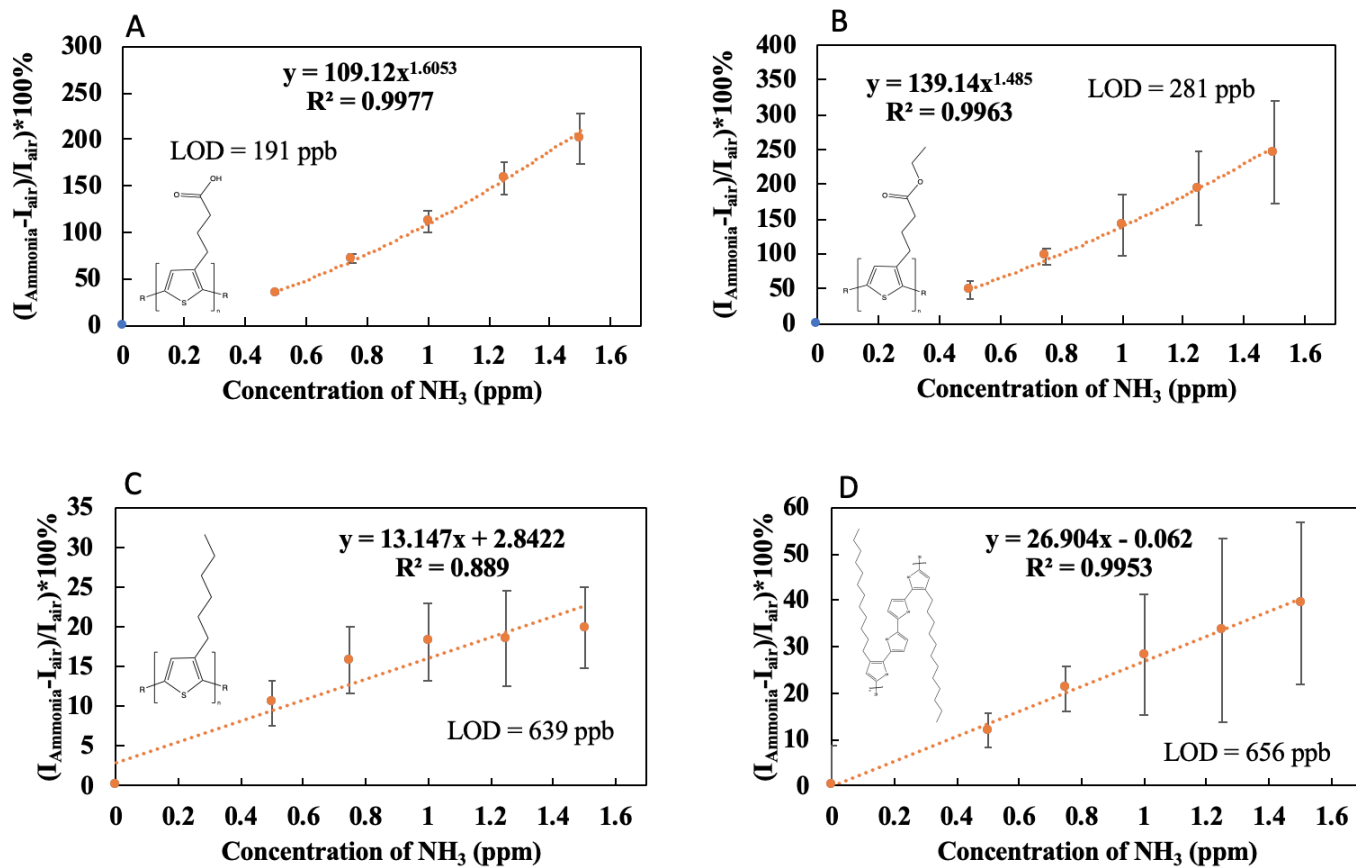
Figure S5. Theoretical Extraction of LOD for each polymer sensing layer A) PT-COOH, B) PT-COOR, C) P3HT, D) PQT12 with exposure to various concentrations of NH_3 for 3 minutes before each consecutive measurement under continuous flow analysis. Slope represents sensitivity response % per ppm.
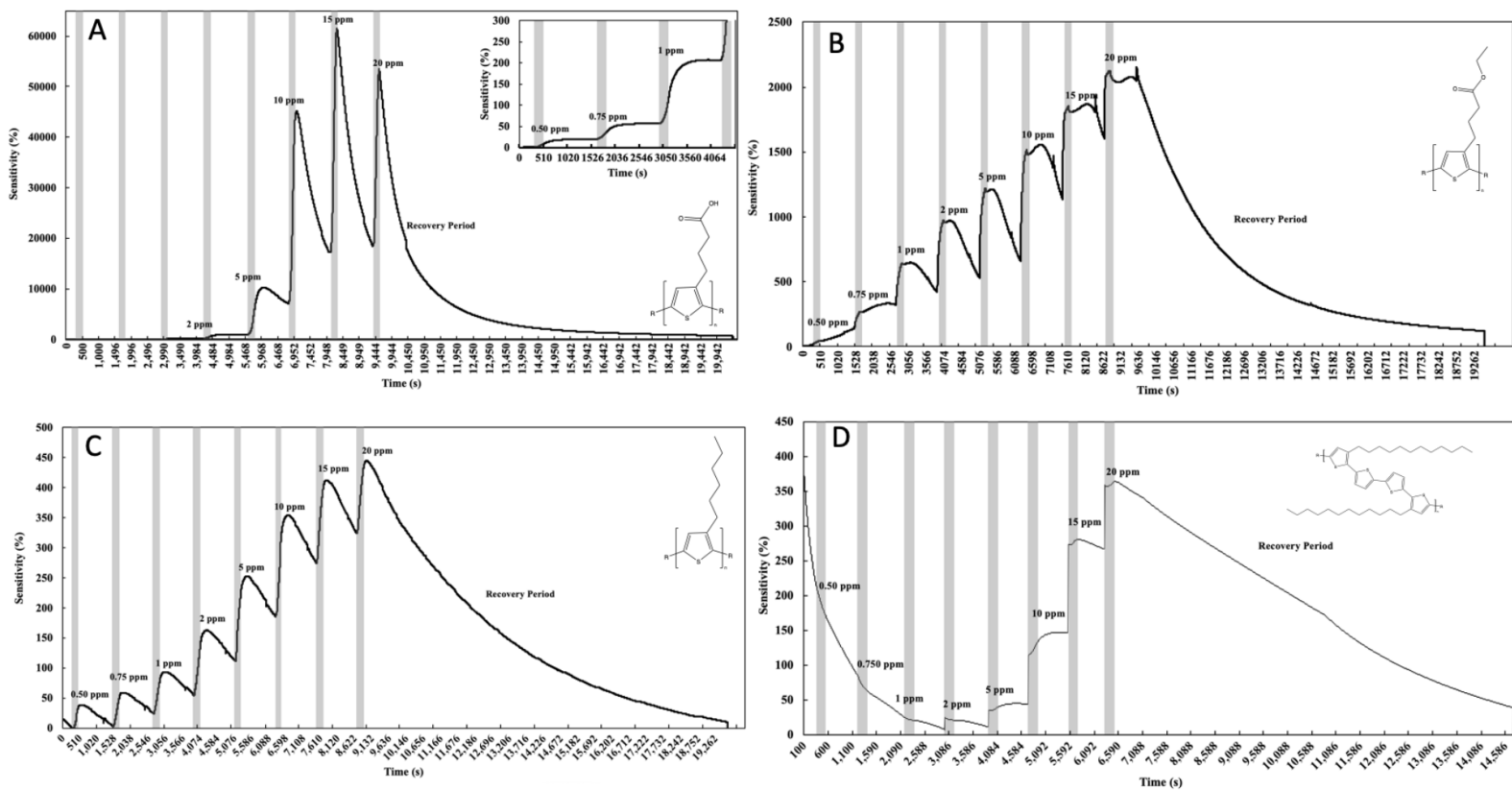
Figure S6. Real time sensitivity and recovery response of A) PT-COOH, B) PT-COOR, C) P3HT, D) PQT12 with devices exposed to continuous flow exposure of NO$_2$. Gray area indicates the time span of gas at specific concentration being turned on and then off. The total duration of time is 180 seconds followed by 12 minutes of recovery before re-exposure to subsequent higher gas concentration.

Figure S7. Analysis of recovery response of A) PT-COOH, B) PT-COOR, C) P3HT, D) PQT12 devices after exposure to 20 ppm of NO_2. Best exponential decay fit line was obtained with linear regression being > 90%. Recovery involved allowing device to be exposed to continuous purified air. Half-life formula was obtained where $t = -\ln(2)/k$. This is taking into account that our exponential decay fit follows a $y = A \ast e^{kt}$ model.

Figure S8. Real time sensitivity and recovery analysis of A) PT-COOH and B) PT-COOR with devices exposed to continuous gas flow of NH_3. Gray area indicates the time span of gas at specific concentration being turned on and then off. The total duration of time is 180 seconds followed by 12 minutes of recovery before 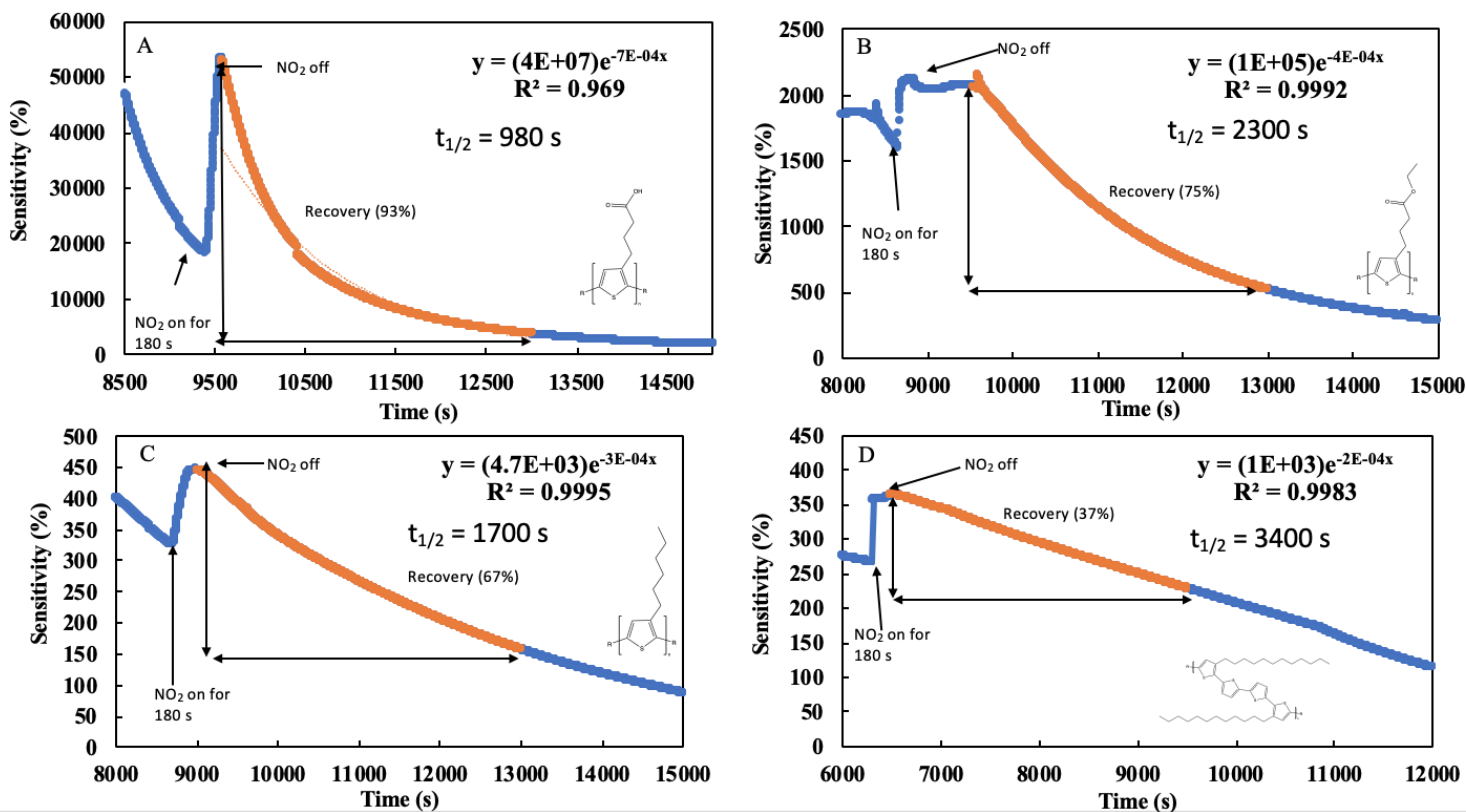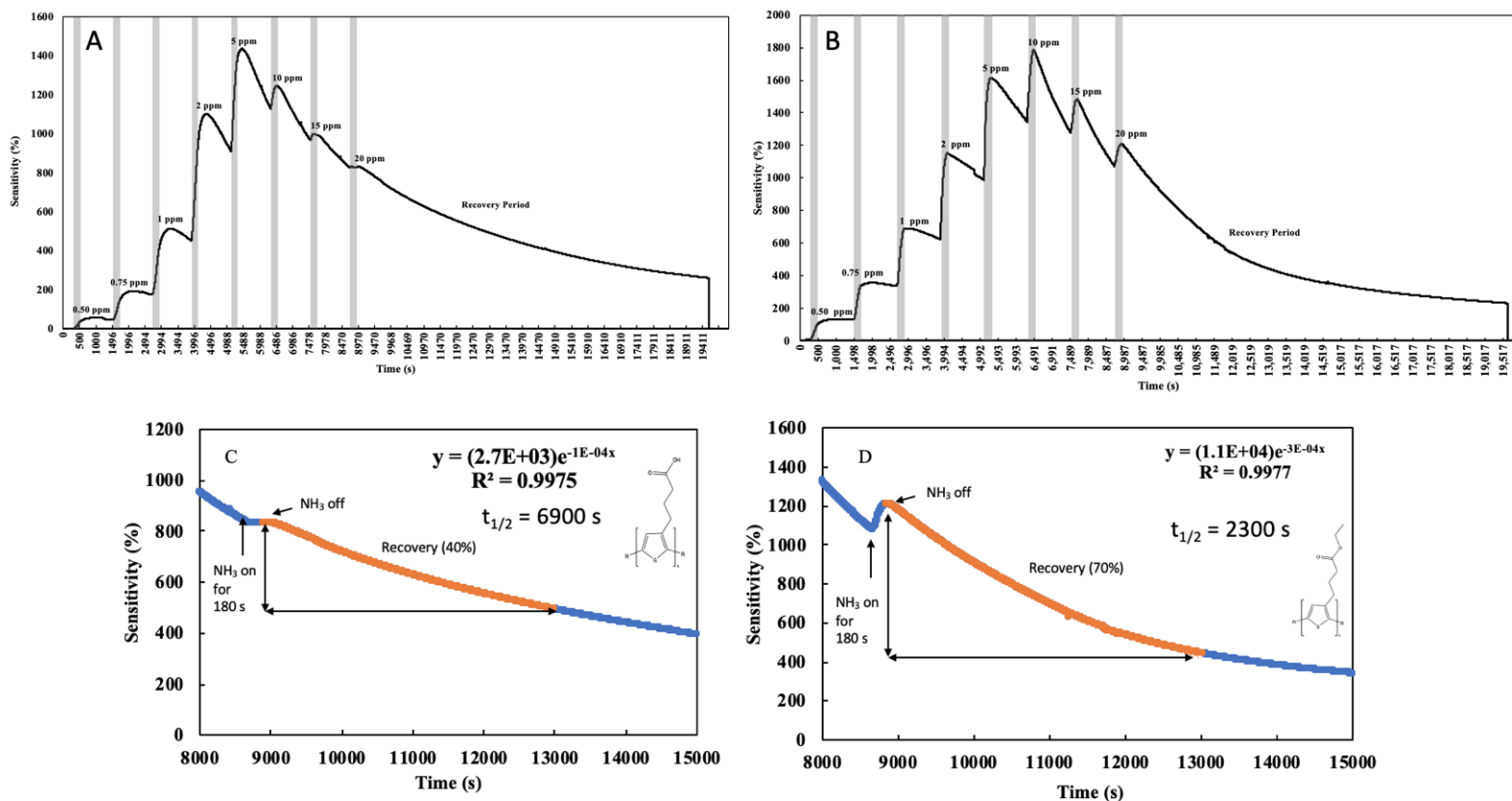re-exposure to subsequent higher gas concentration. Best exponential decay fit line was obtained with linear regression being > 90%. Recovery involved allowing device to be exposed to continuous purified air. Half-life formula was obtained where $t = - \ln(2)/k$. This is taking into account that our exponential decay fit follows a $y = A*e^{kt}$ model.

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Line of Best Fit	Polymer Sensing Layer LOD Determination NO_2 Exposure			
	PT-COOH	PT-COOR	P3HT	PQT12
Linear	200 ppb	557 ppb	740 ppb	1.3 ppm
Power	365 ppb	545 ppb	556 ppb	863 ppb
Linearizing Power Function	226 ppb	679 ppb	750 ppb	1.04 ppm
Average LOD	260 $\pm$ 90 ppb	590 $\pm$ 70 ppb	680 $\pm$ 110 ppb	1.1 $\pm$ 0.2 ppm

Line of Best Fit	Polymer Sensing Layer LOD Determination NH_3 Exposure			
	PT-COOH	PT-COOR	P3HT	PQT12
Linear	99.4 ppb	242 ppb	639 ppb	656 ppb
Power	191 ppb	281 ppb	656 ppb	602 ppb
Linearizing Power Function	254 ppb	471 ppb	1.4 ppm	1.3 ppm
Average LOD	180 $\pm$ 80 ppb	330 $\pm$ 120 ppb	900 $\pm$ 400 ppb	850 $\pm$ 400 ppb

LOD Extraction from Linear Plot

$$LOD = \frac{3 \cdot (\text{Standard Deviation of lowest concentration})}{Slope} * 1000\ \frac{ppb}{ppm}$$

**LOD Extraction from Power Plot**

$$LOB = Mean_{Blank} + 1.645 \cdot (\text{Standard Deviation of the Blank})$$

$$\text{Limit of \%Sensitivity} = LOB + 1.645 \cdot (\text{Standard Deviation of lowest concentration})$$

$$LOD = \text{Insert limit of \% Sensitivity into best fit power function to obtain LOD concentration}$$

Table S2. Limit of detection determination for PT-COOH, PT-COOR, P3HT, and PQT12 under the exposure of NO_2 and NH_3. For the generated calibration curve either fit a linear function or power function in order to extract LOD. In addition, converted a non-linear power function to a linear function to obtain LOD. If best fit line was linear response used the formula presented above utilizing the slope. However, for the power function, incorporated the limit of the blank and obtained limit of % Sensitivity in order to plug into original power equation to obtain LOD.
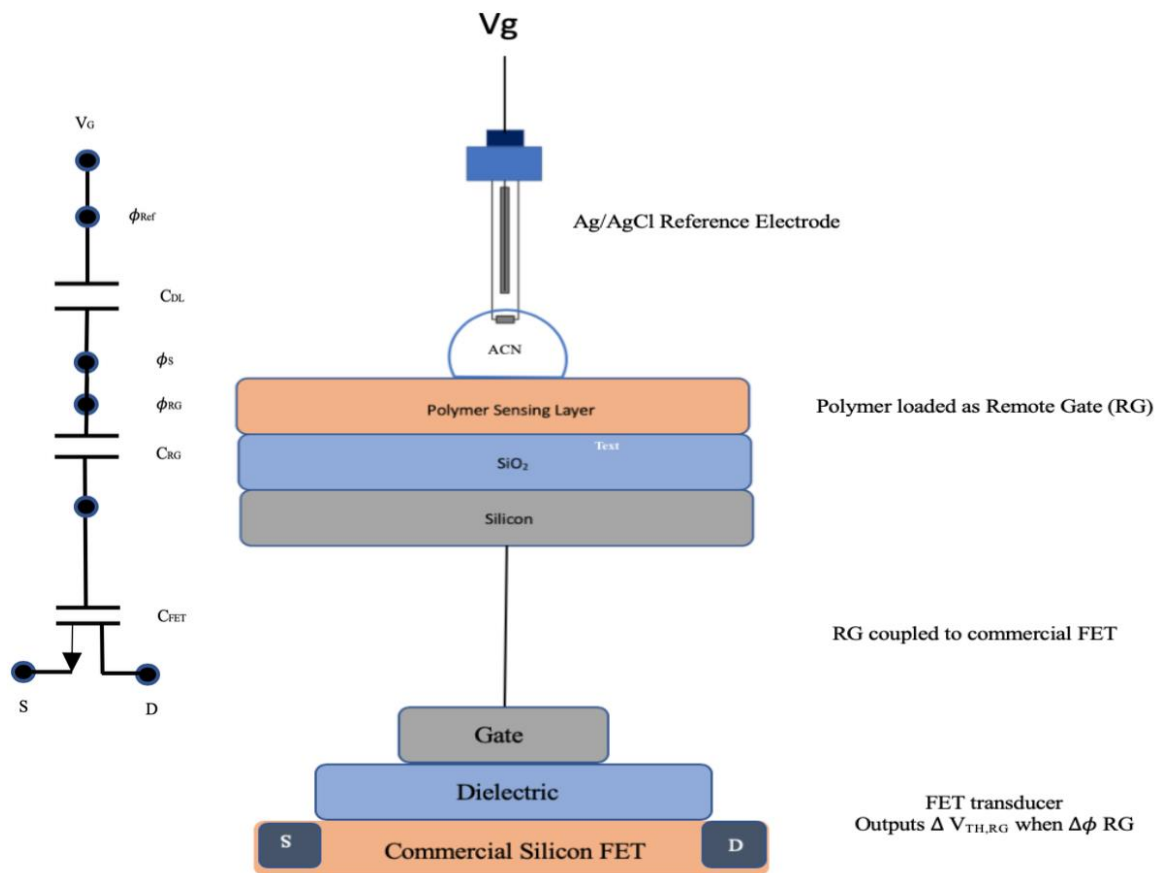
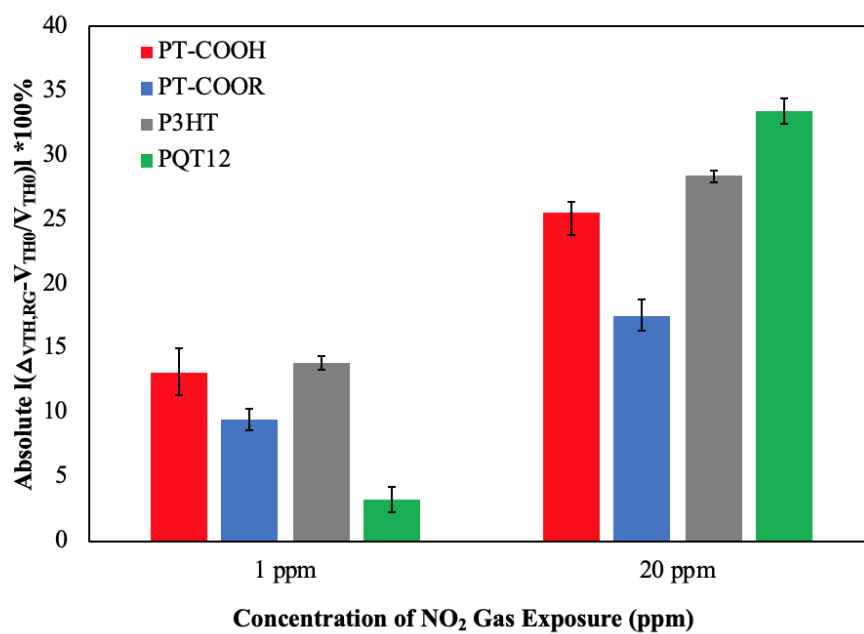Scheme S2. RG FET system and equivalent circuit model for gas sensing quantification detection system.

Figure S9. $V_{TH,Rg}$ sensitivity of polymer sensing layer with exposure to NO_2 (1 ppm and 20 ppm) using RG platform voltage shift analysis.
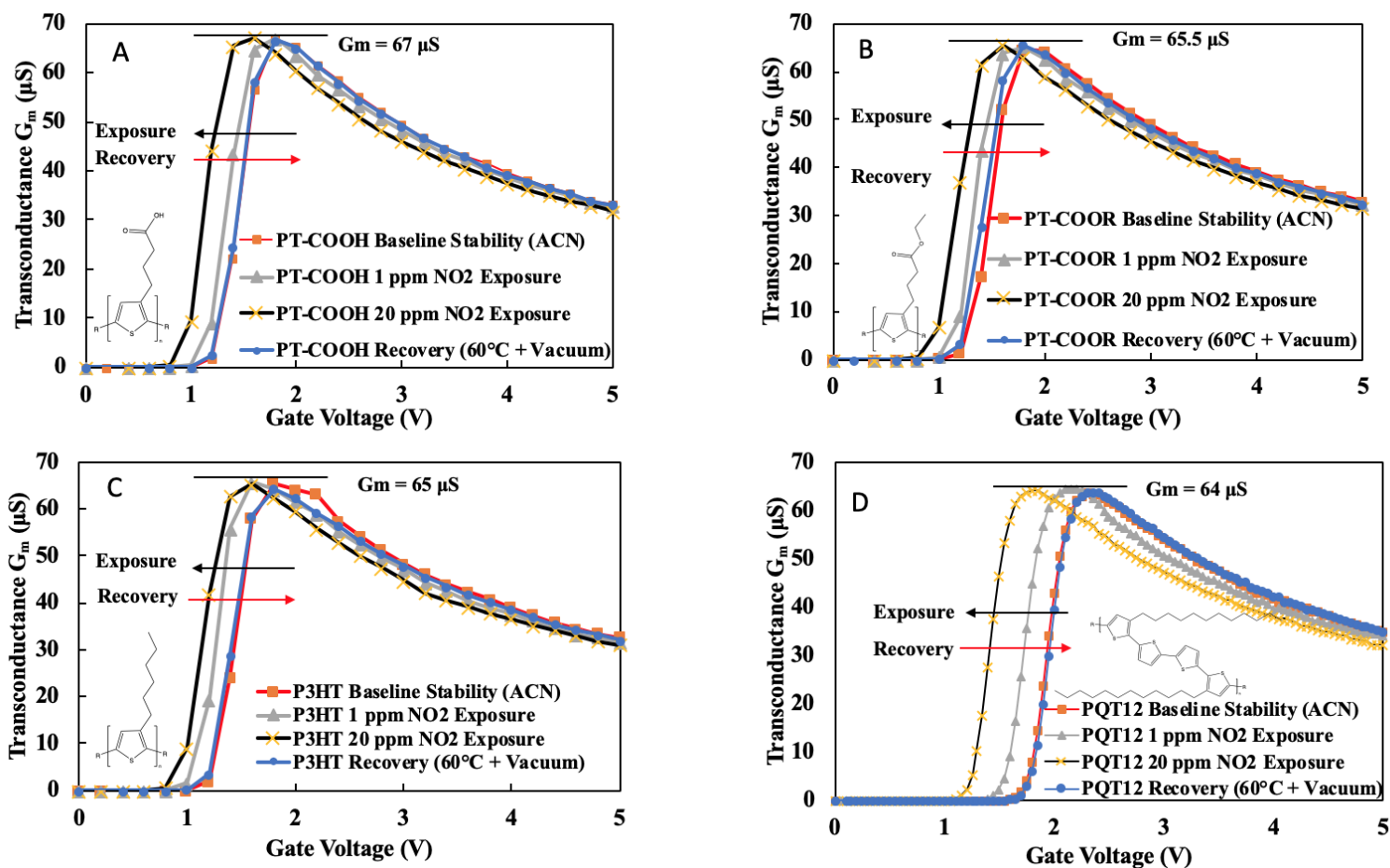
Figure S10. G_m distribution of polymer sensing layer A) PT-COOH, B) PT-COOR, C) P3HT, D) PQT12 with ACN as stability point and exposure with NO_2 (1 ppm and 20 ppm); as well as recovery analysis using RG platform voltage shift analysis.
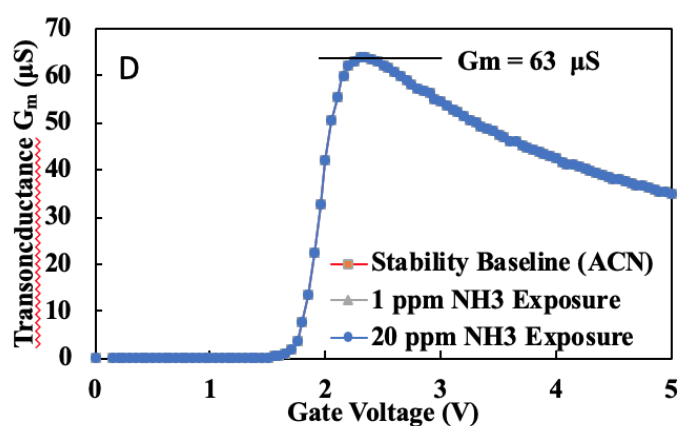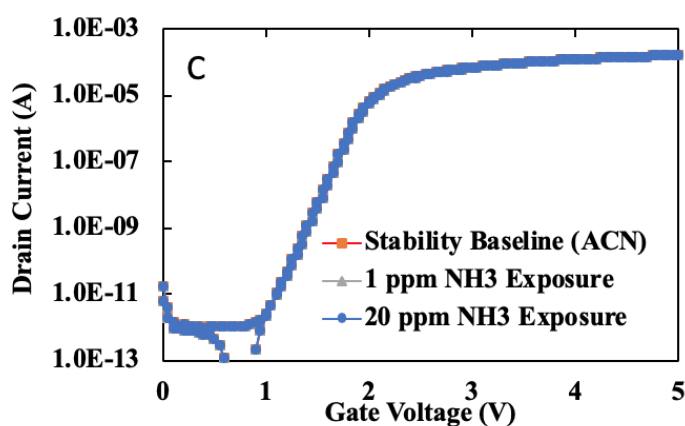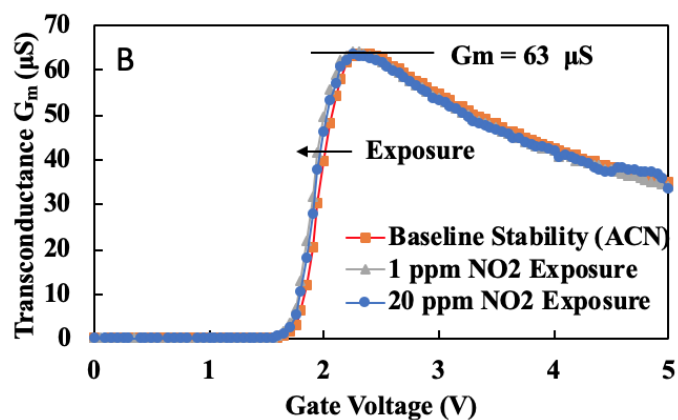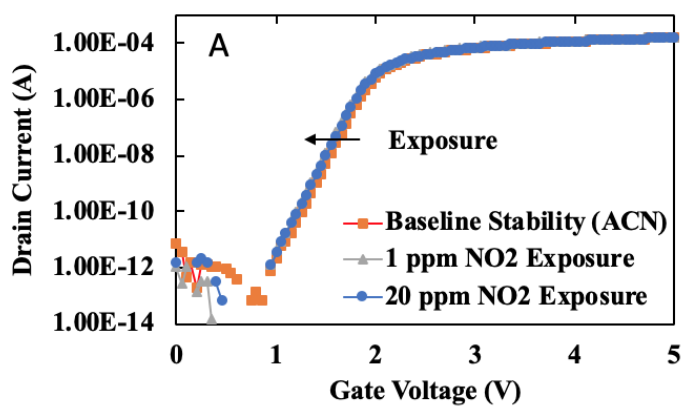
Figure S11. A,B) $V_{TH,RG}$ and C,D) G_m of control surface analysis of Si/SiO$_2$ (300 nm) surface with ACN as stability point and exposure to NO$_2$ (1 ppm and 20 ppm) and NH$_3$ (1 ppm and 20 ppm) using RG platform voltage shift analysis.

Samples	Gas	Concentration	σ (S/cm)	$\Delta V_{th, RG}$ (V)	p (cm^{-3}): RG	μ (cm2/Vs) : RG
PT-COOH	-	No Exposure	7.20E-02 $\pm$ 0.01	-	1.34×10^{19} $\pm$ 3.1×10^{18}	1.98×10^{-2} $\pm$ 7.0×10^{-3}
	NO_2	1 ppm	7.56E-01 $\pm$ 0.04	-0.15 $\pm$ 0.02	6.5×10^{21} $\pm$ 2.6×10^{21}	2.75×10^{-1} $\pm$ 9.8×10^{-2}
	NH_3	1 ppm	4.12E-01 $\pm$ 0.1	-	-	-
PT-COOR	-	No Exposure	1.85E-02 $\pm$ 3E-03	-	7.1×10^{18} $\pm$ 8.5×10^{17}	1.7×10^{-2} $\pm$ 1.8×10^{-3}
	NO_2	1 ppm	5.97E-02 $\pm$ 0.01	-0.11 $\pm$ 0.01	5.1×10^{20} $\pm$ 6.1×10^{19}	5.3×10^{-2} $\pm$ 5.9×10^{-3}
	NH_3	1 ppm	4.37E-02 $\pm$ 0.01	-	-	-
P3HT	-	No Exposure	1.05E-03 $\pm$ 3E-05	-	4.3×10^{19} $\pm$ 7.8×10^{18}	1.6×10^{-4} $\pm$ 3.1×10^{-5}
	NO_2	1 ppm	2.08E-03 $\pm$ 1E-03	-0.07 $\pm$ 0.01	4.9×10^{20} $\pm$ 1.5×10^{20}	3.1×10^{-4} $\pm$ 6.2×10^{-5}
	NH_3	1 ppm	1.00E-03 $\pm$ 1E-04	-	-	-
PQT12	-	No Exposure	1.00E-3 $\pm$ 4E-04	-	1.3×10^{19} $\pm$ 4.9×10^{18}	5.4×10^{-4} $\pm$ 2.3×10^{-4}
	NO_2	1 ppm	1.04E-03 $\pm$ 5E-04	-0.05 $\pm$ 0.02	9.2×10^{19} $\pm$ 3.5×10^{19}	5.6×10^{-4} $\pm$ 2.4×10^{-4}
	NH_3	1 ppm	8.00E-04 $\pm$ 2E-05	-	-	-

Table S3. Electrical parameters consisting of conductivity, $\Delta V_{TH, RG}$, hole concentrations of polymer sensing layer before and after 1 ppm exposure of NO_2 due to calculating the voltage shift occurrence with the incorporation of the RG FET platform. $\Delta V_{TH, RG}$ was calculated by taking the average value of $V_{TH, RG}$ from four trials. Mobility for unexposed devices was obtained from FET measurements, while mobility for NO_2-exposed devices was calculated based on hole concentrations obtained by using $\sigma = e * \mu_h * p_0$. Initial hole concentration was obtained from μ_h from OFET using transfer curve and conductivity (σ).

Polymerization:
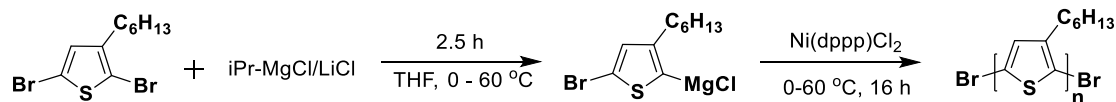
2,5-dibromo-3-hexylthiophene (500 mg, 1.53 mmol) was added to 8 mL anhydrous THF under N_2, then purge and fill with N_2 for three times. 0.92 mL isopropylmagnesium chloride (2 M in THF) was added to the solution of LiCl (64.9 mg, 1.53 mmol), then the complex solution was added dropwise to the solution of 2,5-dibromo-3-hexylthiophene at 0 ℃, 0.5 h later, the solution was heated to 60 ℃ and stirred for 2 h. After solution cooled to 0 ℃, catalyst $Ni(dppp)Cl_2$ (24.3 mg, 3% eq.) was added under N_2. 10 min later, the solution was heated to 60 ℃ and stirred about 16 h. The reaction mixture was precipitated into a well-stirred solution of methanol (100 mL) and stirred for 10 min. The resulting suspension was filtered with filter paper and extracted (Soxhlet) with acetone for 3 days and dried under vacuum to afford a dark solid.
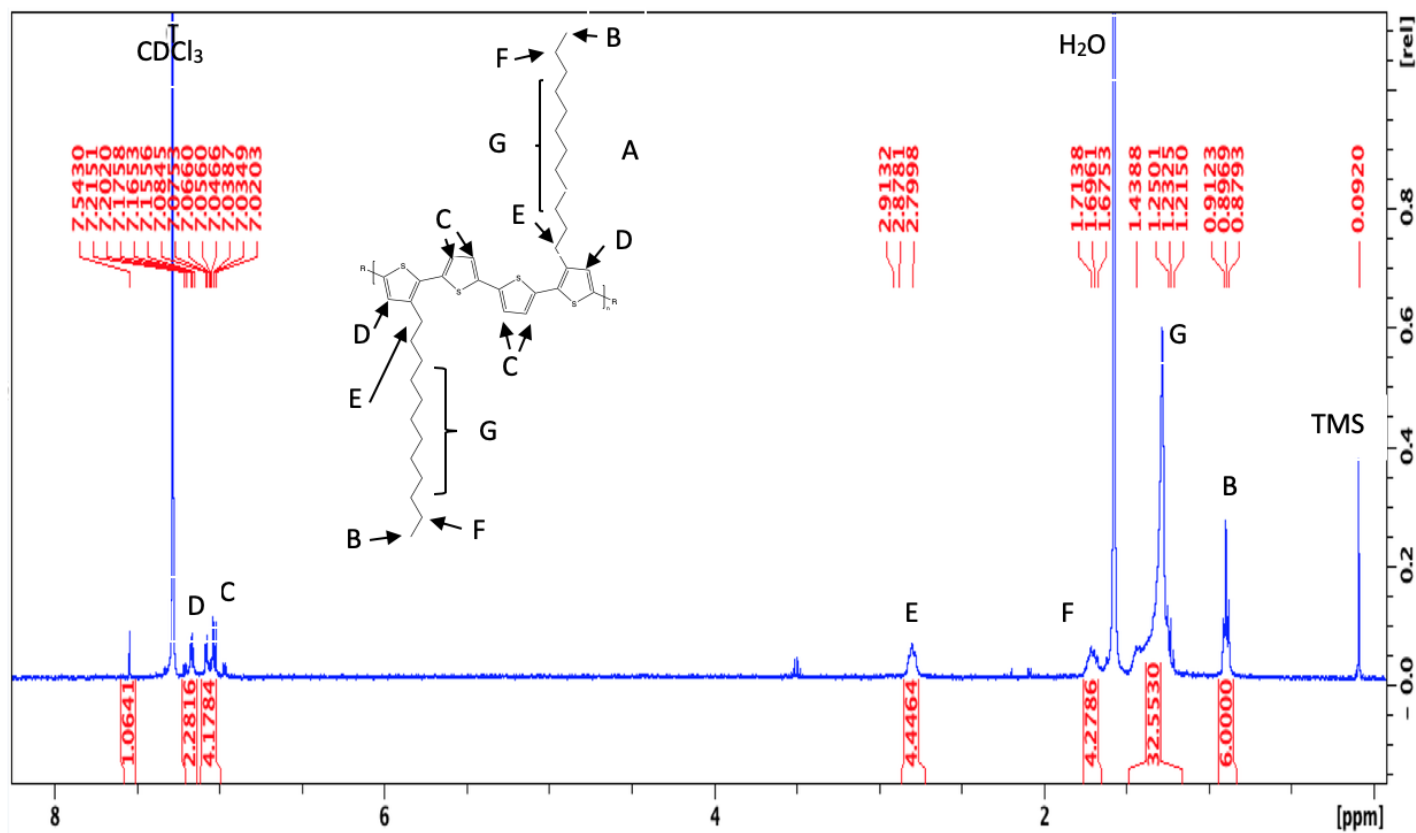
NMR Spectra:

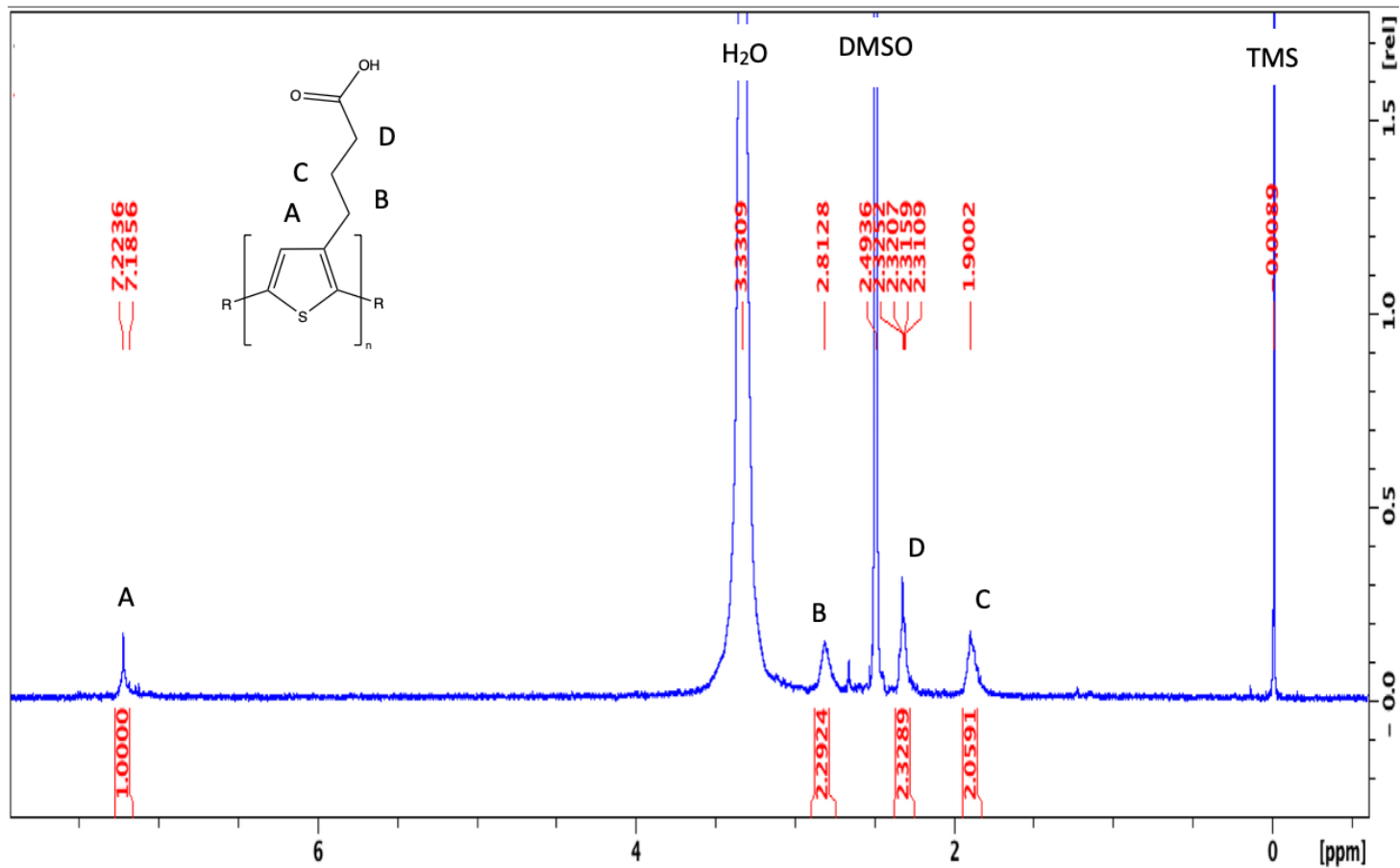**Poly(3-hexylthiophene-2,5-diyl)regioregular (P3HT)**
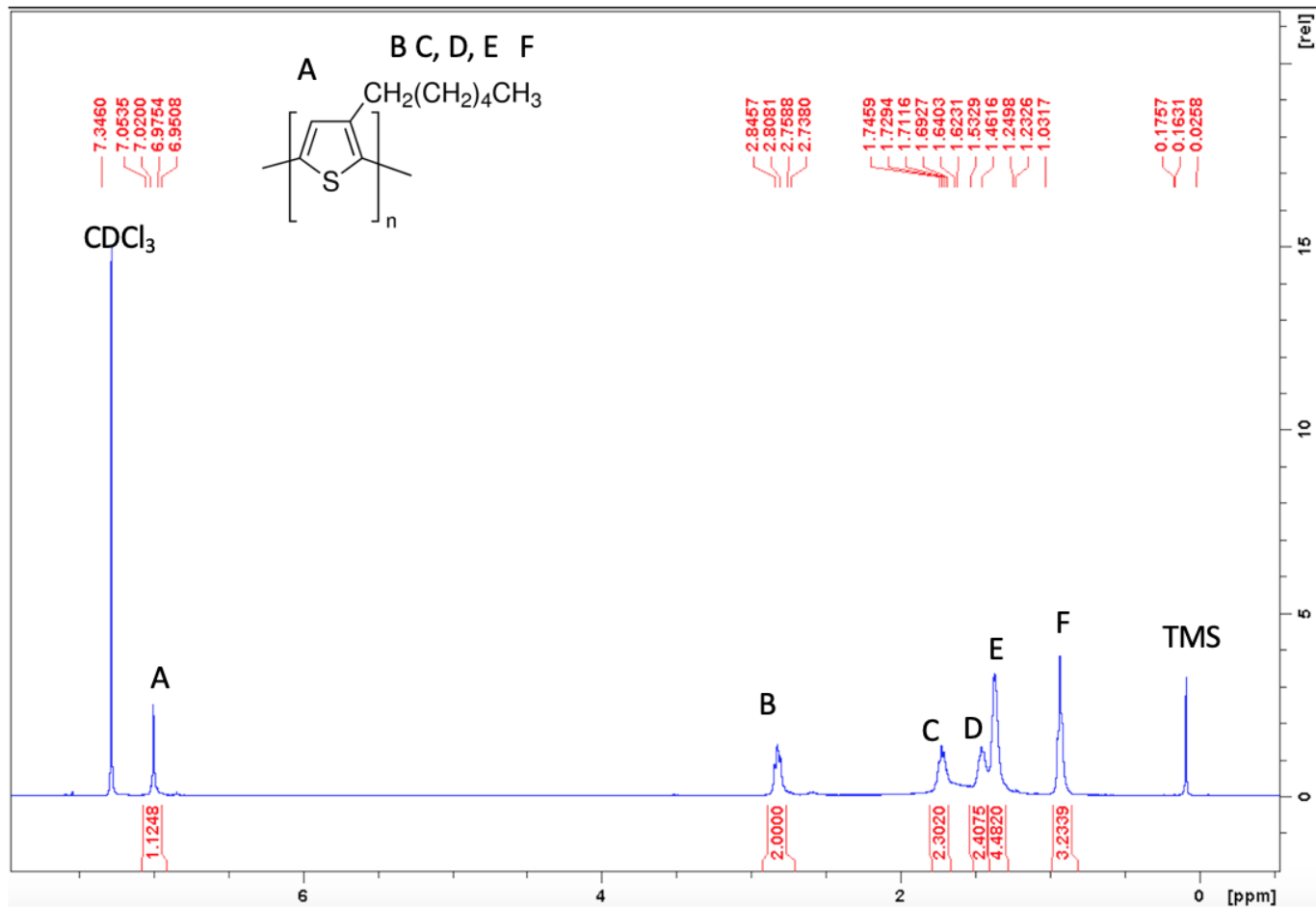
^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.03 (t, 3H), 1.23-1.25(m, 4H), 1.46-1.53 (m, 2H), 1.62-1.75 (m, 2H) 2.74-2.85(t, 2H), 6.98 (s, 1H).

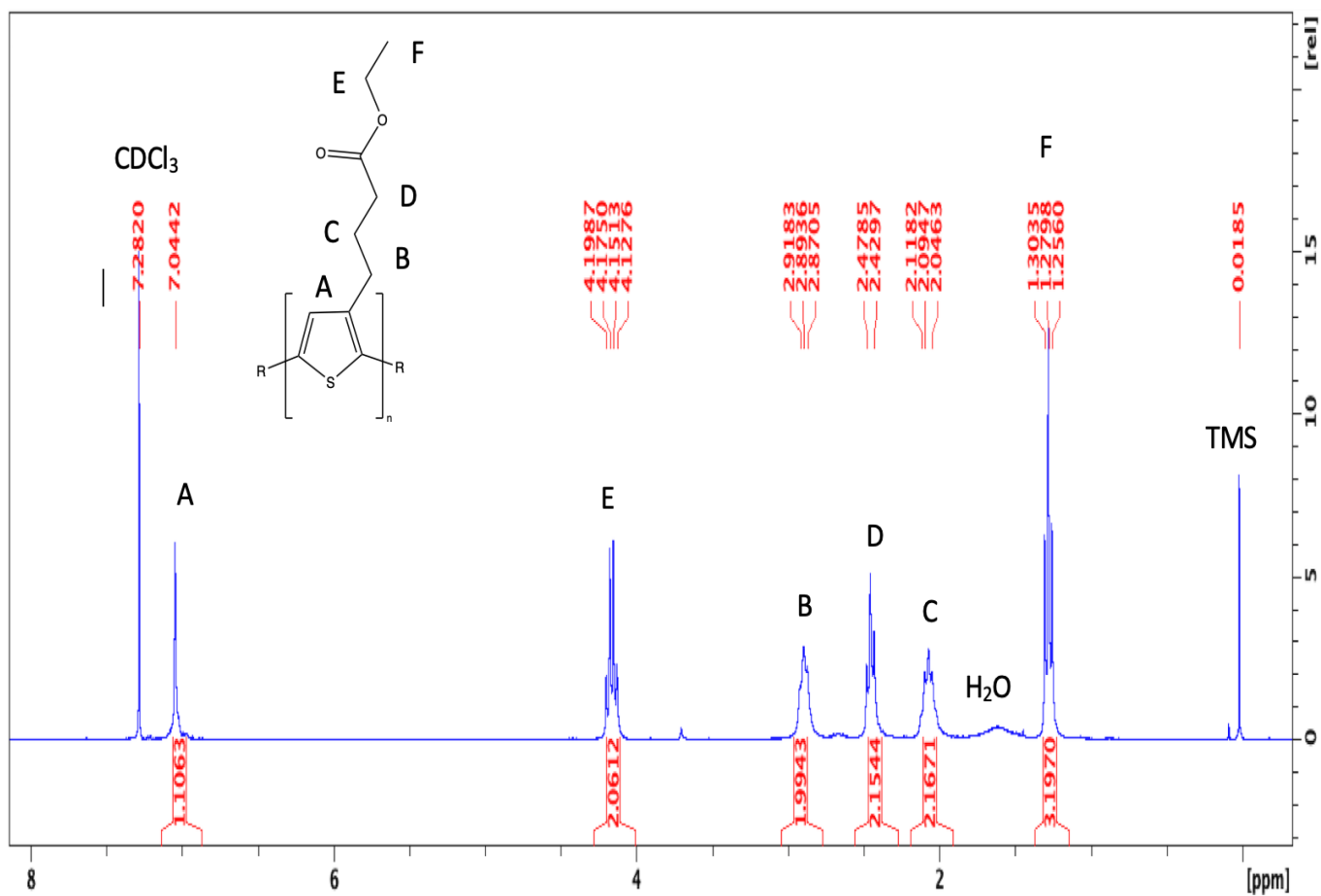**Poly(3,3''' -didodecyl quarter thiophene) (PQT12)**

^{1}H NMR (300 MHz, Chloroform-*d*) δ 0.88-0.91 (t, 6H), 1.2-1.4(m, 32H), 1.67-1.71 (m, 4H), 2.8-2.91 (m, 4H) 7.02-08(m, 4H), 7.17-7.21 (d, 2H).

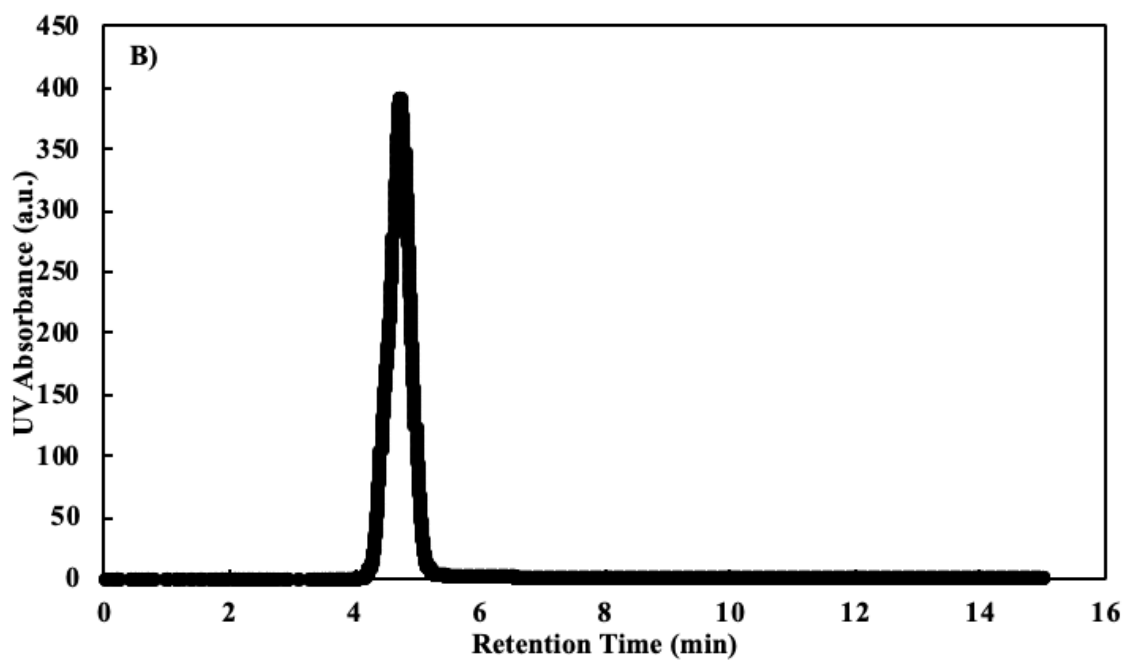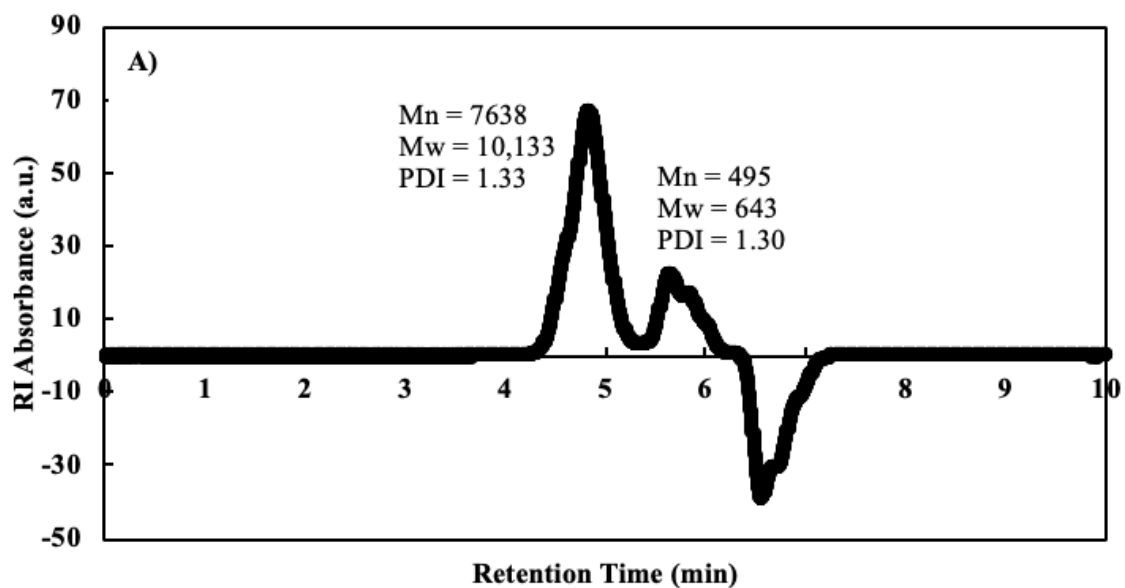**Poly[3-(3-Carboxypropyl)thiophene-2,5-diyl]regioregular (PT-COOH)**

^{1}H NMR (300 MHz, DMSO-*d6*) δ 1.90 (m, 2H), 2.3-2.5(m, 2H), 2.81 (m, 2H), 7.18-7.22 (d, 1H).

3.4 Poly[3-(Ethyl-4-butanoate)thiophene-2,5-diyl]regioregular (PT-COOR)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.26-1.30 (t, 3H), 2.05-2.12(m, 2H), 2.43-2.48 (m, 2H), 2.87-2.92 (m, 2H) 4.13-4.20(t, 2H), 7.04 (s, 1H).

Gel Permeation Chromatography (GPC):

A) RI and B) UV SEC trace of Poly(3-hexylthiophene-2,5-diyl)regioregular after polymerization and purification.