Electronic Supplementary Information for

Templated approach to well-defined, oxidatively coupled conjugated polymers

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Summary of Schemes, Figures, and Tables

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1. Experimental Section

1.1. Materials

Grubbs' III catalyst (Grubbs Catalyst© M300, dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II)) was purchased from Sigma Aldrich and used as received. HPLC grade tetrahydrofuran stabilized with butylated hydroxy toluene (BHT) was purchased from Fisher Scientific. All other reagents and solvents were purchased from Sigma-Aldrich and were used as received. Dry dichloromethane was obtained from an Innovative Technology PureSolv solvent purification system. Schlenk techniques were employed for experiments conducted under argon, and glovebox techniques were employed for experiments conducted under nitrogen.

1.2. Experimental Methods

Nuclear magnetic resonance (NMR) spectra were obtained at room temperature using a Varian Mercury 400 spectrometer (400 MHz), Agilent DD2-500 spectrometer (500 MHz), or Agilent DD2-600 spectrometer (600 MHz) and were referenced to residual chloroform or a TMS internal standard. nb-OMeEDOT, nb-OHx, P(OMeEDOT), and P(OMeEDOT-*b*-OHx) were characterized by ^{1}H, ^{13}C{^{1}H} NMR, and 2D NMR (HSQC, HMBC, COSY) spectroscopy. P(OMePEDOT) polymers with low degrees of oxidative coupling and P(OMePEDOT-*b*-OHx) polymers were characterized by ^{1}H NMR spectroscopy only, due to solubility limitations. ^{1}H NMR spectra were used to calculate the % of oxidative coupling in P(OMePEDOT) and P(OMePEDOT-*b*-OHx) polymers (**Fig. S8**), and to calculate the block ratio in P(OMeEDOT-*b*-OHx) polymers (**Fig. S22**).

Mass spectra were recorded on a JEOL AccuTOF Plus 4G model JMS-T1000LP mass spectrometer equipped with a Direct Analysis in Real Time (DART) ion source. Elemental analysis (C, H, N) was obtained using a Flash 2000 CHNS analyzer.

Fourier transform infrared (IR) spectroscopy was performed using PerkinElmer Spectrum 100 FT-IR or Thermo Scientific iS50 spectrometers equipped with attenuated total reflection crystals. IR spectra were baseline corrected and, where possible, normalized to 80% transmittance for ester carbonyl absorptions bands ($\nu_{C=O} \sim 1730$ cm^{-1}). Differentiated IR spectra were calculated from baseline corrected and/or normalized IR spectra using Plot2 for Mac OS.

Size exclusion chromatography was carried out using gel permeation chromatography (GPC) instruments. Samples dissolved in tetrahydrofuran (THF) were filtered through a 0.1 μm

PTFE membrane and characterized using a Tosoh EcoSEC HLC-8320 instrument with a dual-flow refractive index detector. HPLC grade, BHT-stabilized THF with 2.5 g/L tetrabutylammonium bromide additive was used as an eluent at a temperature of 40 °C and a flow rate of 0.6 mL/min. Molecular weight and dispersity were determined relative to polystyrene standards. Samples dissolved in chloroform were filtered through a 0.2 μm PVDF membrane and characterized using a Waters Breeze instrument with a refractive index detector. Chloroform was used as an eluent at a temperature of 40 °C and a flow rate of 1 mL/min. Molecular weight and dispersity were determined relative to polystyrene standards.

Optical absorption spectra were obtained using Varian Cary 5000 UV-vis-NIR or Lambda 1050 UV/Vis spectrometers. Optical absorption spectra were normalized with respect to absorption bands centered at 257 nm. Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker CW X-band ECS-EMXplus EPR spectrometer and were referenced to 1,1-diphenyl-2-picrylhydrazyl radical (DPPH).

Light scattering experiments were carried out using a Malvern Zetasizer Nano-ZS instrument equipped with a He-Ne laser (λ = 633 nm). Samples were prepared at 0.25 mg/mL and filtered through 0.45 μm glass syringe filters into 10 mm glass cuvettes. No sample was observed on the membrane of the syringe filter after filtration.

Transmission electron microscopy (TEM) samples were prepared by drop-casting one drop (~ 10 μL) of the colloidal solution (0.25 mg/mL) onto a carbon coated copper grid, which was placed on a piece of filter paper to remove excess solvent. Bright field TEM micrographs were obtained on a HT7700 microscope at an acceleration voltage of 80 kV. No staining of the samples was necessary. Images were analysed using the ImageJ software package developed at the US National Institute of Health.[1] For statistical length analysis, 270 − 280 micelles were carefully traced by hand to determine the diameter. From this data, the average diameter and standard deviation were calculated.

1.3. Computational Methods

Density functional theory calculations were performed with Gaussian 09.[2] Geometry optimizations and subsequent frequency calculations were carried out using the B3LYP[3,4] functional with the 6-31G(d)[5] basis set. Calculated frequencies were multiplied by a scale factor of 0.9613 for B3LYP/6-31G(d) calculations.[6]

1.4. Synthesis

nb-OMeEDOT Synthesis. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (0.5 g, 2.9 mmol), hydroxymethyl EDOT (1.0 g, 5.9 mmol), 4-(dimethylamino)pyridine (0.04 g, 0.3 mmol), and a stir bar were dried under vacuum in a flame-dried flask. The flask was backfilled with argon, and dry dichloromethane (25 mL) was added by syringe. The resulting solution was stirred and cooled in an ice water bath, then *N*-ethyl-*N′*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl, 0.6 g, 2.9 mmol) was added to the flask. The water bath was allowed to warm to room temperature overnight. After 1 day, the solution was diluted with dichloromethane, and washed with aqueous hydrochloric acid (10% v/v), water, and brine, then dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum to afford a brown, crystalline solid. Purification by column chromatography (chloroform, 1% v/v methanol) afforded a white, crystalline solid. Yield: 1.2 g, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 – 6.37 (m, 4H), 6.21 – 6.25 (m, 2H), 4.16 – 4.43 (m, 8H), 3.99 – 4.08 (m, 2H), 3.08 – 3.20 (m, 2H), 2.63 – 2.75 (m, 2H), 2.02 – 2.11 (m, 1H), 1.50 – 1.55 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 173.3, 141.3, 141.1, 138.1, 100.2, 100.1, 71.5, 65.7, 62.9, 47.3, 46.0, 45.5. HRMS (DART-TOF)$^+$ *m/z*: $[M + H]^+$ calcd for $C_{23}H_{23}O_8S_2$, 491.08289; found, 491.08198. Anal. calcd for $C_{23}H_{22}O_8S_2$, C, 56.32; H, 4.52; N, 0. Found: C, 56.47; H, 4.81; N, 0.00.

nb-OHx. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (1.0 g, 6.1 mmol), 4-(dimethylamino)pyridine (0.08 g, 0.7 mmol), and a stir bar were dried under vacuum in a flame-dried flask. The flask was backfilled with argon, and 1-hexanol (1.7 mL, 13.6 mmol) and dry dichloromethane (20 mL) were added by syringe. The resulting solution was stirred and cooled in an ice water bath, then *N*-ethyl-*N′*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl, 1.2 g, 6.2 mmol) was added to the flask. The water bath was allowed to warm to room temperature overnight. After 1 day, the solution was diluted with dichloromethane, washed with aqueous hydrochloric acid (10% v/v), water, and brine, then dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum to afford a yellow oil. Purification by column chromatography (dichloromethane) afforded a yellow-tinted liquid that was used without further purification. Yield: 1.8 g, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.84 – 5.99 (m, 2H), 3.56 – 3.85 (m, 4H), 2.69 – 2.79 (m, 2H), 2.22 – 2.33 (m, 2H), 1.82 – 1.91 (m, 1H), 1.24 – 1.35 (m, 4H), 1.11 – 1.17 (m, 1H), 0.95 – 1.10 (m, 12H), 0.55 – 0.66 (m, 6H). $^{13}C\{^1H\}$ NMR (126 MHz,

$CDCl_3$): δ 172.6, 137.6, 64.1, 46.8, 45.3, 45.0, 31.2, 28.3, 25.4, 22.2, 13.6. HRMS (DART-TOF)$^+$ *m/z*: [M + H]$^+$ calcd for $C_{21}H_{35}O_4$, 351.25299; found, 351.25281. Anal. calcd for $C_{21}H_{34}O_4$, C, 71.96; H, 9.78; N, 0. Found: C, 72.48; H, 9.36; N, 0.00.

General Procedure for P(OMeEDOT) Synthesis. Under an inert gas atmosphere, Grubbs' III catalyst was dissolved in a minimal amount of dichloromethane and added quickly to a solution of nb-OMeEDOT in dichloromethane ([nb-OMeEDOT] = 25 mM, [nb-OMeEDOT]:[cat.] = 50:1, 25:1, or 10:1). The resulting solution was stirred for at least three hours, then excess ethyl vinyl ether was added to the flask and the solution was stirred for at least one hour. The solvent was removed under vacuum to afford a green crystalline solid. Purification by repeated dissolution in chloroform, precipitation into methanol, and isolation via centrifugation, afforded an off-white crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.21 – 6.37 (br, 4H), 5.31 – 5.51 (br, 1H), 5.15 – 5.31 (br, 1H), 4.07 – 4.40 (br, 8H), 3.90 – 4.04 (br, 2H), 3.25 – 3.50 (br, 1H), 2.74 – 3.01 (br, 3H), 1.92 – 2.28 (br, 1H), 1.10 – 1.32 (br, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.0 141.1, 133.0, 100.0, 71.4, 65.5, 62.7, 52.3, 45.9, 40.7.

General Procedure for P(OMeEDOT-*b*-OHx) Synthesis. Under a nitrogen atmosphere, Grubbs' III catalyst was dissolved in a minimal amount of dichloromethane and added quickly to a solution of nb-OMeEDOT in dichloromethane ([nb-OMeEDOT] = 12 mM, [nb-OMeEDOT]:[cat.] = 25:1). The resulting solution was stirred for at least three hours, then a solution of nb-OHx in dichloromethane ([nb-OHx] = 20 mM, [nb-OHx]:[cat.] = 5:1, 15:1, 25:1, or 50:1) was added to the flask and the solution was stirred for at least three hours. Ethyl vinyl ether was then added to the flask and the solution was stirred for at least one hour. The solvent was removed under vacuum to afford a green crystalline solid. Purification by repeated dissolution in chloroform, precipitation into methanol, and isolation via centrifugation, afforded an off-white or green-tinted crystalline solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.24 – 6.35 (br, 4H), 5.34 – 5.48 (br, 2H), 5.15 – 5.28 (br, 2H), 4.08 – 4.38 (br, 8H), 3.91 – 4.05 (br, 6H), 3.26 – 3.47 (br, 2H), 2.74 – 3.04 (br, 6H), 1.93 – 2.27 (br, 2H), 1.56 – 1.62 (br, 4H), 1.24 – 1.36 (br, 12H), 1.09 – 1.24 (br, 2H), 0.85 – 0.93 (br, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.3, 141.2, 132.8, 100.0, 71.4, 66.6, 64.8, 63.0, 52.8, 45.5, 40.7, 32.3, 28.5, 26.6, 23.1, 14.0.

General Procedure for P(OMePEDOT) Synthesis. Iron (III) *p*-toluenesulfonate hexahydrate ([Fe(III)] = 0.23 or 23 mM) was added to a solution of P(OMeEDOT) in dichloromethane ([OMeEDOT] = 0.05 or 5 mM). The mixture was stirred under ambient atmosphere, for a given time (t = 0.5 – 8 days), at a given temperature (rt, 25 °C, or 60 °C). Excess iron (III) *p*-toluenesulfonate was removed through one of two general procedures: **A** ([OMeEDOT] = 0.05 mM) or **B** ([OMeEDOT] = 5 mM).

General Procedure for hydroxymethyl PEDOT synthesis. Iron (III) *p*-toluenesulfonate hexahydrate ([Fe(III)] = 23 mM) was added to a solution of hydroxymethyl EDOT in dichloromethane ([OMeEDOT] = 0.05 or 5 mM). The mixture was stirred under ambient atmosphere and temperature for 8 days. Excess iron (III) *p*-toluenesulfonate was removed through one of two general procedures: **A** ([HOMeEDOT] = 0.05 mM) or **B** ([HOMeEDOT] = 5 mM).

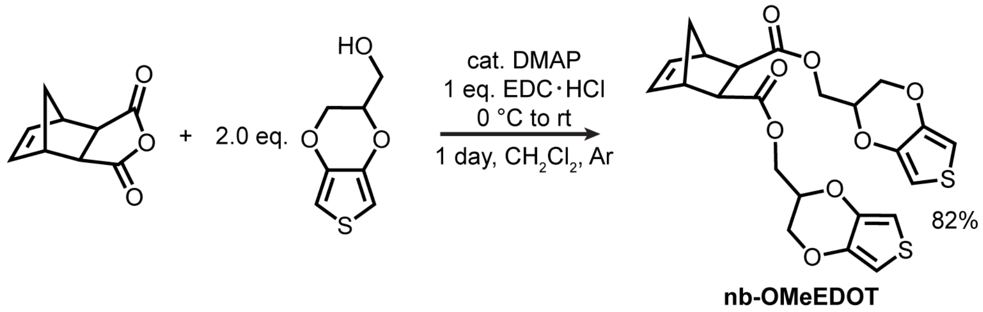
General Procedure A for Oxidative Coupling Purification. The crude mixture was washed with water and brine, treated with excess ammonia (2 M in methanol), and the solvent was removed under vacuum. To remove residual salts, the crude polymer was washed with water:methanol (5:2 v/v), collected by vacuum filtration, washed with water and methanol, and dried under vacuum.

General Procedure B for Oxidative Coupling Purification. The crude sample was collected by vacuum filtration, washed with solvent (chloroform, methanol, water), treated with excess ammonia (2 M in methanol), and dried under vacuum.

General Procedure for P(OMePEDOT-*b*-OHx) Synthesis. Iron (III) *p*-toluenesulfonate hexahydrate ([Fe(III)] = 23 mM) was added to a solution of P(OMeEDOT-*b*-OHx) in dichloromethane ([OMeEDOT] = 0.05 mM). The mixture was stirred under ambient atmosphere and temperature for 4 days. The crude mixture was washed with water, an aqueous solution of disodium ethylenediaminetetraacetate dihydrate (0.05 M), and brine, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.33 – 5.52 br, 2H), 5.15 – 5.33 (br, 2H), 3.47 – 4.52 (br, 14H), 3.27 – 3.51 (br, 2H), 2.65– 3.11 (br, 6H), 1.98– 2.23 (br, 2H), 1.61 – 1.95 (br, 4H), 1.04 –1.45 (br, 14H), 0.65 –1.04 (br, 6H).

2. P(OMePEDOT) Homopolymers

2.1. nb-OMeEDOT Monomer



Scheme S1. nb-OMeEDOT synthesis.

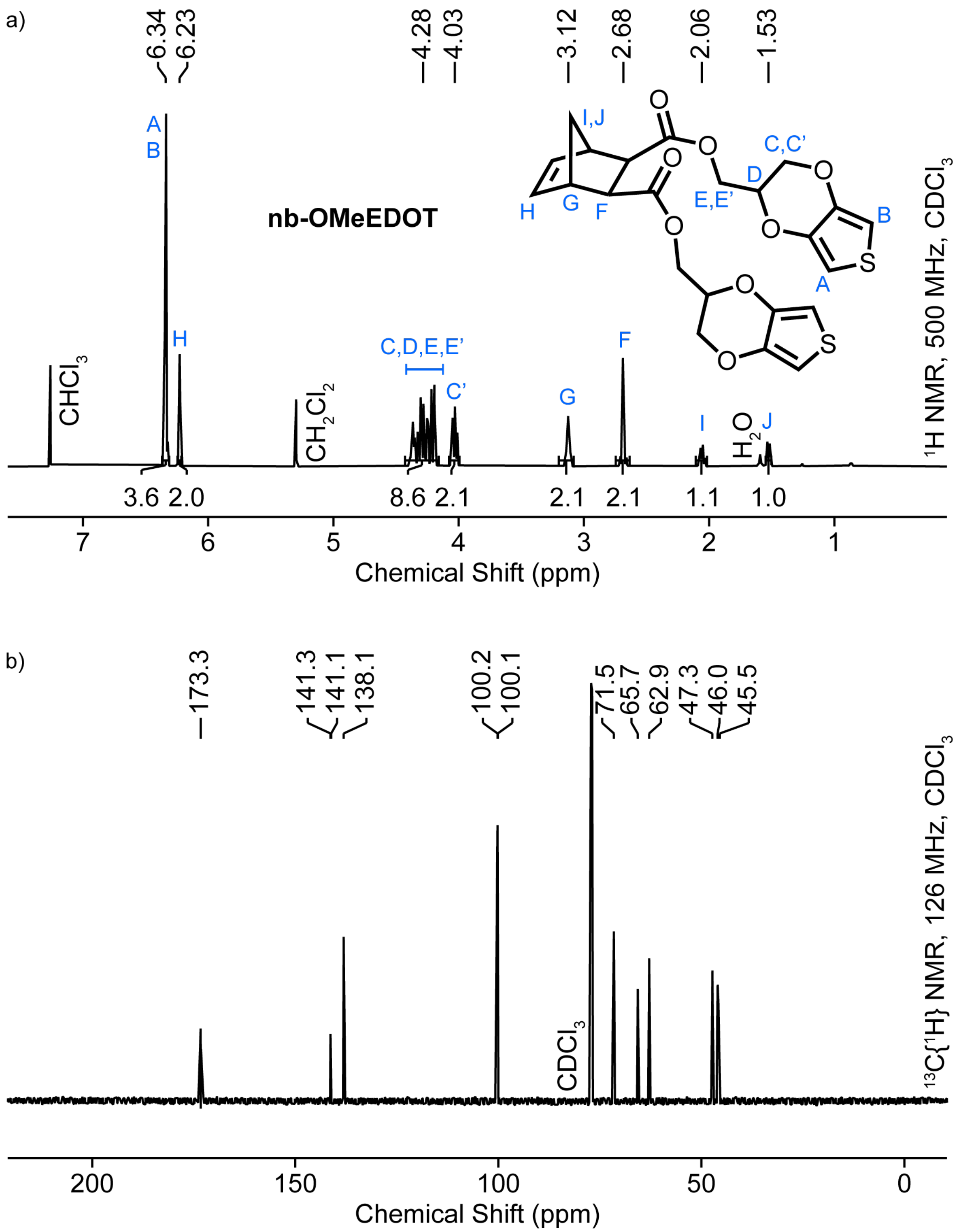


Fig. S1 a) ^{1}H and b) $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, rt) spectra of nb-OMeEDOT.

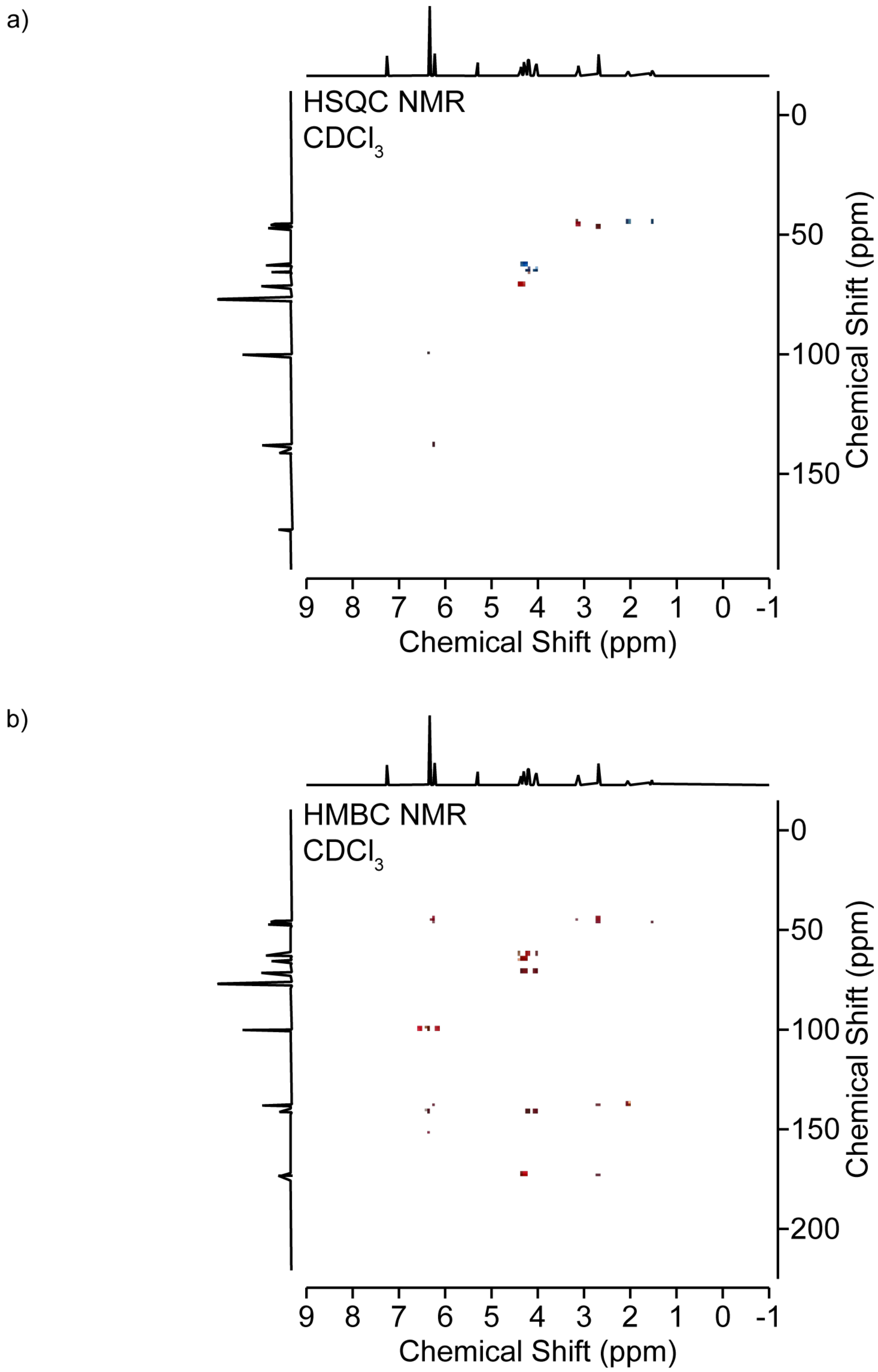


Fig. S2 a) HSQC and b) HMBC NMR ($CDCl_3$, rt) spectra of nb-OMeEDOT.

a)

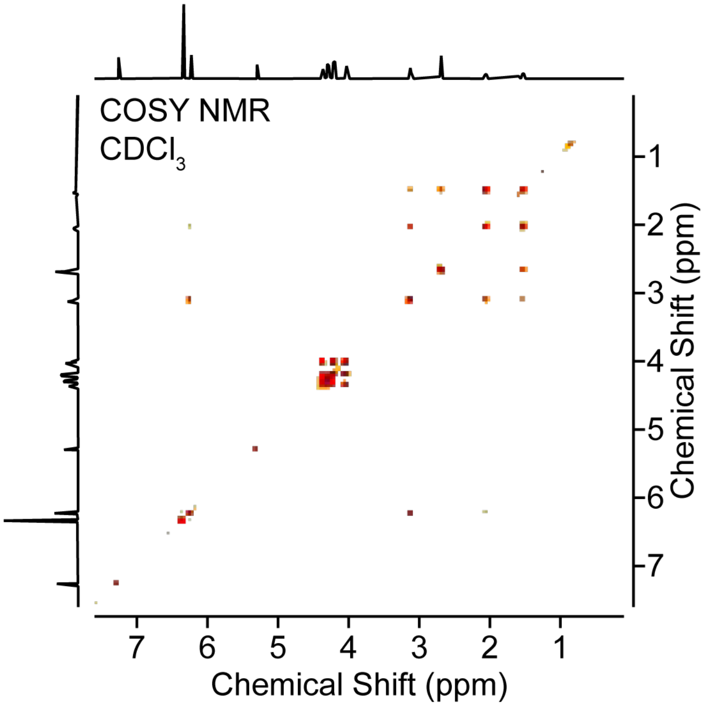


Fig. S3 COSY NMR ($CDCl_3$, rt) spectrum of nb-OMeEDOT.

2.2. P(OMeEDOT) Homopolymers

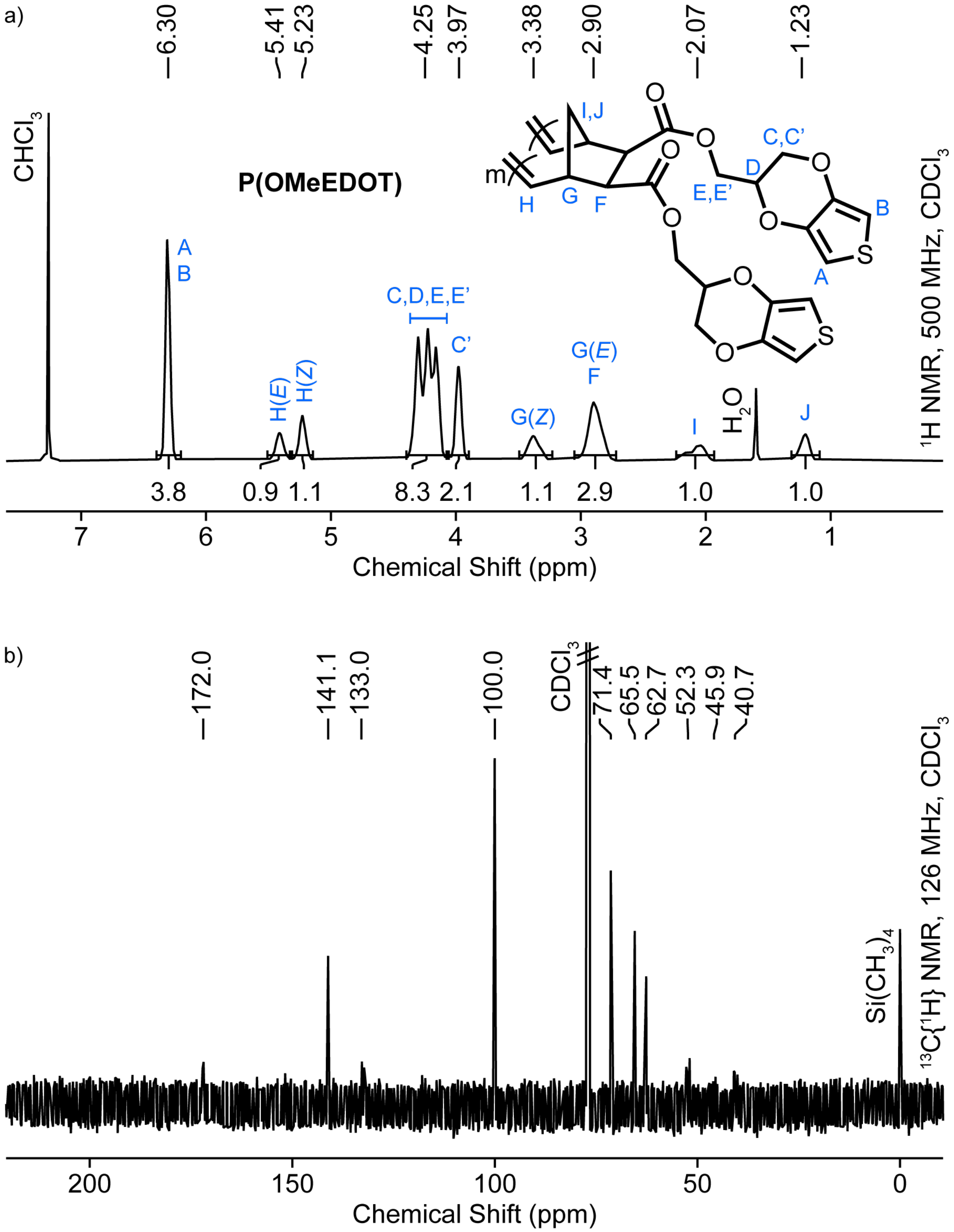
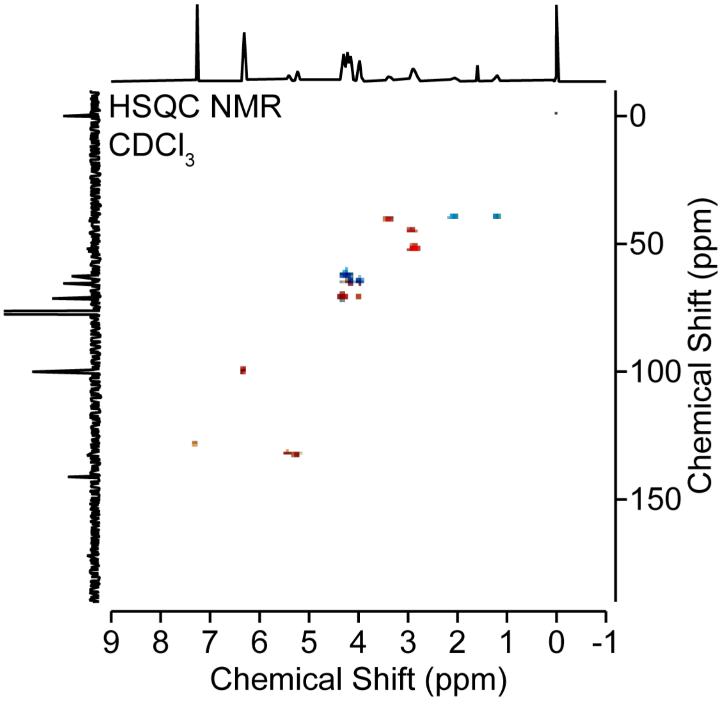


Fig. S4 Representative a) ^{1}H and b) ^{13}C{^{1}H} NMR ($CDCl_3$, rt) spectra of P(OMeEDOT)$_{25}$, featuring a mixture of *E* (45%) and *Z* (55%) olefins.

a)



b)

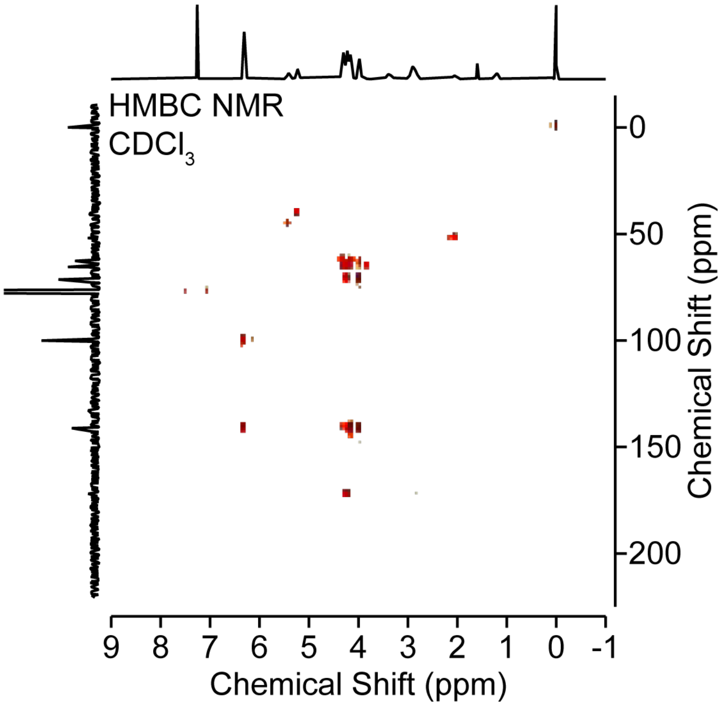


Fig. S5 Representative a) HSQC and b) HMBC NMR ($CDCl_3$, rt) spectra of $P(OMeEDOT)_{25}$.

Table S1. Summary of P(OMeEDOT) reaction conditions and properties.

No.	Polymer	[nb-OMeEDOT]:[cat.][a]	$M_{\text{n, GPC}}$[b] (kg/mol)	$X_{\text{n, GPC}}$[c]	$Đ_{\text{GPC}}$[b]	% yield
1[d]	P(OMeEDOT)$_{50}$	50:1 (52:1)	26.7	54	1.13	97
2[d]	P(OMeEDOT)$_{25}$	25:1 (22:1)	10.9	22	1.20	81
3[e]		25:1 (24:1)	10.3	21	1.10	97
4[d]	P(OMeEDOT)$_{10}$	10:1 (10:1)	6.0	12	1.65	53

[a] Approximate values. Experimental molar ratios are provided in parentheses.

[b] THF GPC measured at 40 °C, calibrated against polystyrene standards.

[c] $X_{\text{n, GPC}} = \frac{M_{\text{n, GPC}}}{\mathrm{M}_{\text{OMeEDOT}}}$, where $\mathrm{M}_{\text{OMeEDOT}} = 491$ g/mol.

[d] Synthesis conducted on a Schlenk line under an argon atmosphere.

[e] Synthesis conducted in a glovebox under a nitrogen atmosphere.

2.3. P(OMePEDOT) Homopolymers

2.3.1. Sample Calculations and Analysis

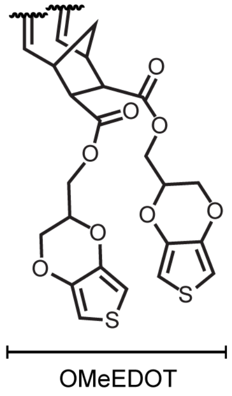


Fig. S6 Monomer unit definition, OMeEDOT, for P(OMeEDOT).

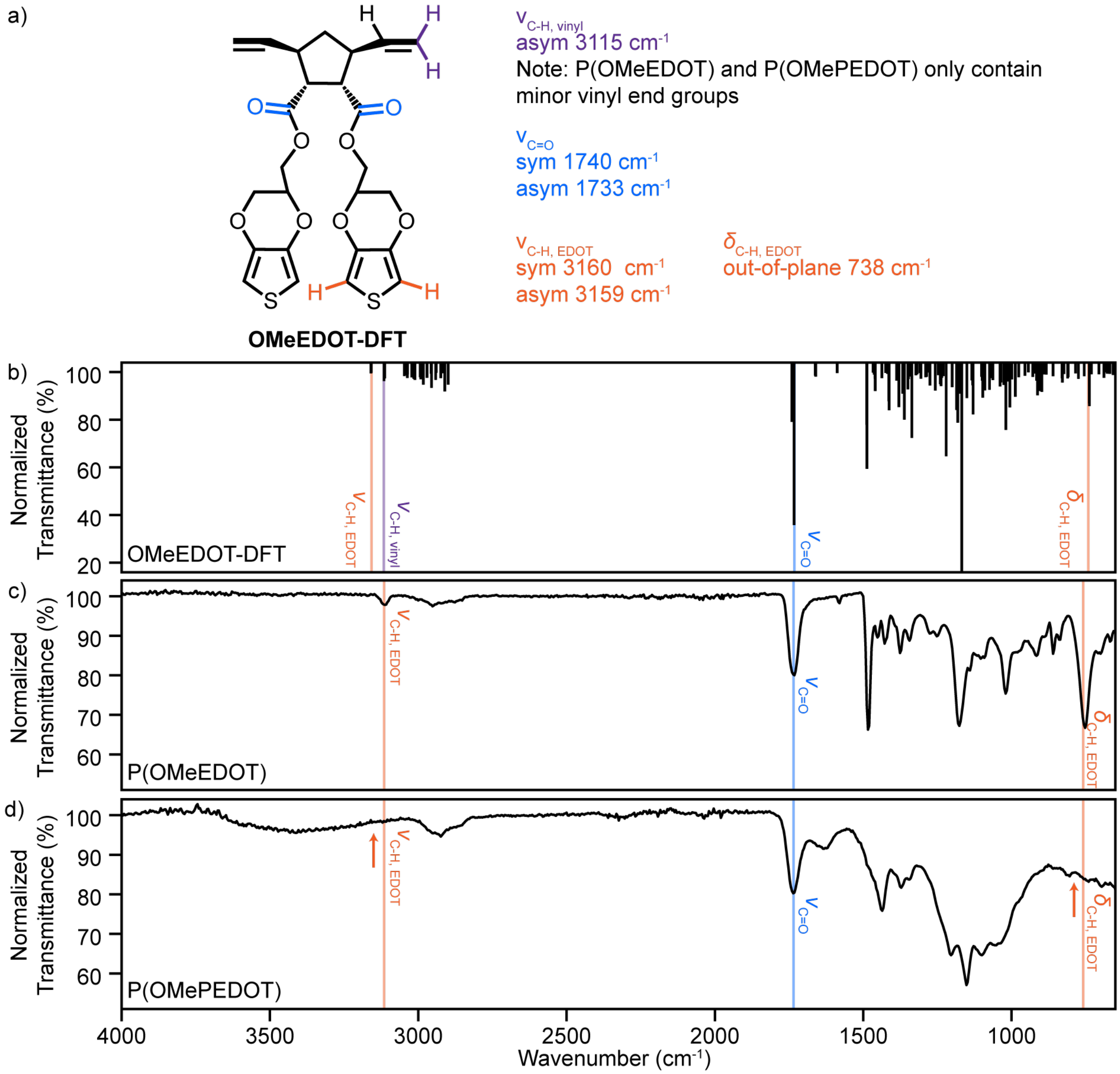
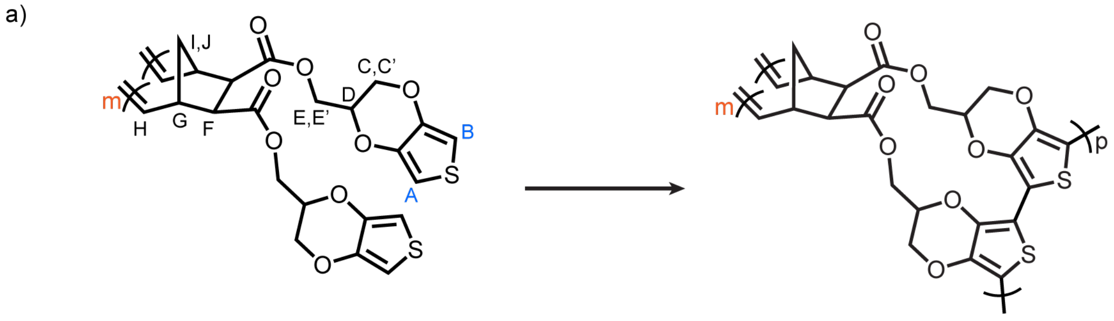


Fig. S7 Qualitative IR analysis of the degree of oxidative coupling in P(OMePEDOT) polymers. a) DFT calculated vibrational frequencies of a model compound, OMeEDOT-DFT, featuring characteristic aromatic EDOT stretches and deformations (C–H, EDOT), and carbonyl stretches (C=O). Vinyl stretching frequencies (C–H, vinyl) are calculated for the model monomer, but are only minorly relevant to the end groups of P(OMeEDOT) and P(OMePEDOT) polymers. b) DFT calculated vibrational frequency spectra, c) representative P(OMeEDOT) IR spectra, and d) representative P(OMePEDOT) IR spectra, indicating aromatic EDOT and carbonyl absorption bands.



P(OMeEDOT)

P(OMePEDOT)

b)
$$\%\ \text{Conversion} = \frac{\text{Actual Degree of Oxidative Coupling}}{\text{Maximum Degree of Oxidative Coupling}} \cdot 100\%$$

$$\text{Maximum Degree of Oxidative Coupling} = \frac{\text{Maximum H Lost}}{\text{Total H}} = \frac{2(2m - 1)}{2(2m)} \approx \frac{2(2X_n - 1)}{2(2X_n)}$$

$$\text{Actual Degree of Oxidative Coupling} = \frac{H_{A,B,\ \mathrm{P(OMeEDOT)}} - H_{A,B,\ \mathrm{P(OMePEDOT)}}}{H_{A,B,\ \mathrm{P(OMeEDOT)}}}$$

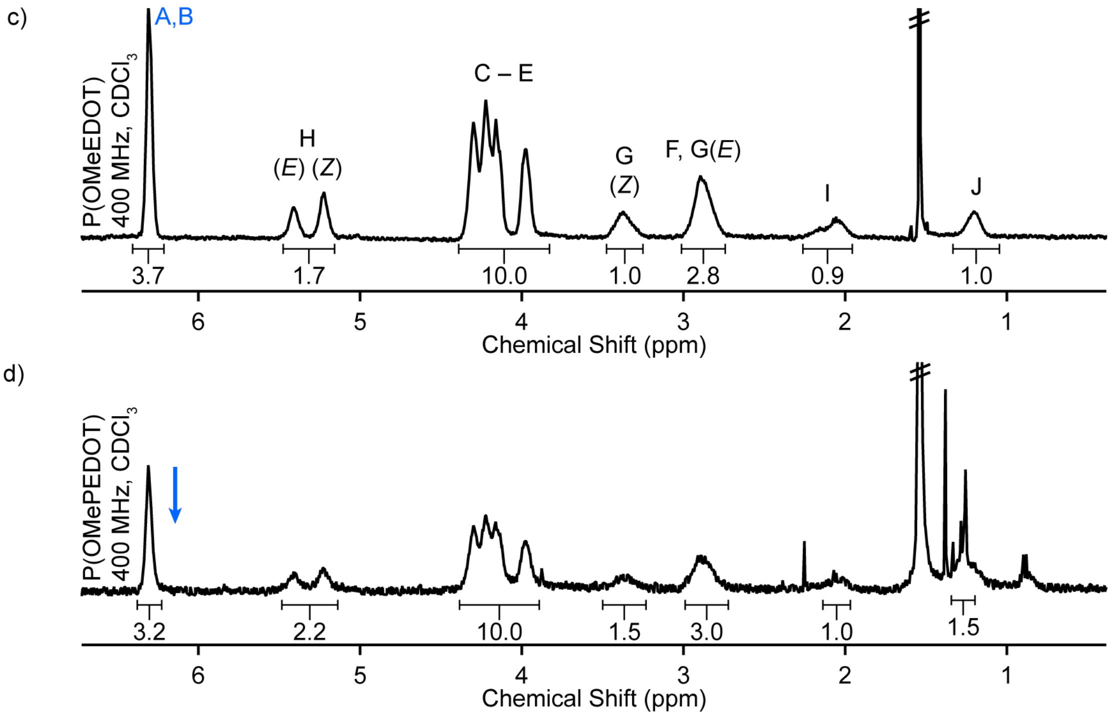


Fig. S8 Quantitative ^{1}H NMR analysis of the degree of oxidative coupling in P(OMePEDOT) polymers. a) P(OMeEDOT) and P(OMePEDOT) proton labels for ^{1}H NMR analysis. The loss of aromatic EDOT protons, H_A and H_B, that are displaced during oxidative coupling is used to quantify the degree of oxidative coupling. b) Sample calculation for the degree of oxidative coupling in P(OMePEDOT), comparing H_A and H_B integrations in c) P(OMeEDOT) and d) P(OMePEDOT) ^{1}H NMR spectra.

2.3.2. Optimization Studies

Table S2. Summary of P(OMePEDOT) starting materials, reaction conditions, and properties.

No.	P(OMeEDOT) Starting Material	Oxidative Coupling Reaction Conditions				P(OMePEDOT) Oxidative Coupling Product			
		[OMeEDOT][a] (mM)	[Fe(III)][a] (mM)	T (°C)	t (days)	Crude Mixture Appearance	$CHCl_3$ Solubility[b]	% conversion[c]	% yield
1	$P(OMeEDOT)_{25}$ Table S1, No. 2	0.05 (0.05)	0.23 (0.25)	25	1	Yellow, clear solution	Very soluble	7	71
2					4	Green, clear solution	Very soluble	28	
3					8	Colorless, blue solid	Partially soluble	N/A	
4	$P(OMeEDOT)_{25}$ Table S1, No. 2	0.05 (0.05)	0.23 (0.24)	60	1	Blue, blue solid	Partially soluble	N/A	-
5					4	Blue, blue solid	Partially soluble	N/A	
6					8	Colorless, blue solid	Partially soluble	N/A	
7	$P(OMeEDOT)_{25}$ Table S1, No. 3	0.05 (0.05)	23 (24)	rt[d]	0.5	Green-tinted yellow, yellow solid	Very soluble	13	75
8		0.05 (0.05)	23 (23)		1	Green-tinted yellow, yellow solid	Partially soluble	N/A	77
9		0.05 (0.05)	23 (24)		2	Green-yellow, yellow solid	Partially soluble	N/A	50
10		0.05 (0.05)	23 (23)		4	Green, blue and yellow solid	Insoluble	N/A	62
11		0.05 (0.05)	23 (23)		8	Green, blue and yellow solid	Insoluble	N/A	14

[a] Approximate values. Experimental molar ratios are provided in parentheses. Monomer unit, OMeEDOT, defined in **Fig. S6**.

[b] Very soluble: > 10 mg/mL; partially soluble: some solvation for ~ 0.01 mg/mL; insoluble: no significant solvation at any concentration.

[c] Calculated from ^1H NMR spectra ($CDCl_3$, rt), for fully soluble polymers. For sample calculation see **Fig. S8**.

[d] Experiments conducted at room temperature (approx. 18 – 24 °C)

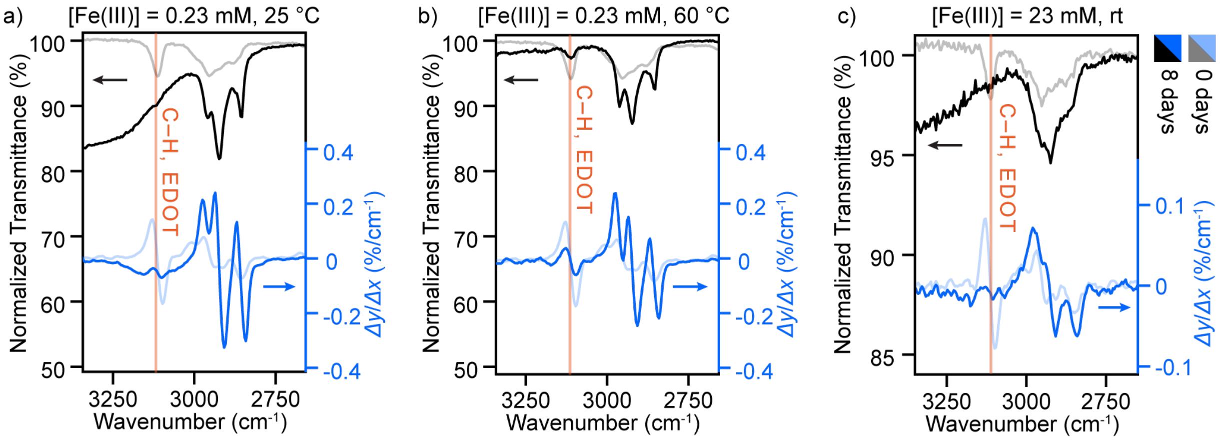


Fig. S9 Normalized IR spectra (black) and differentiated IR spectra (blue) of templated oxidative polymerization optimization studies. P(OMeEDOT) oxidative coupling was compared under ambient and elevated temperatures (a vs. b), and stoichiometric and excess oxidant concentrations (a vs. c). IR spectra are normalized to ester carbonyl absorptions bands ($\nu_{C=O}$ ~ 1730 cm^{-1}, 80% transmittance). Room temperature (rt) is approximately 18 – 24 °C.

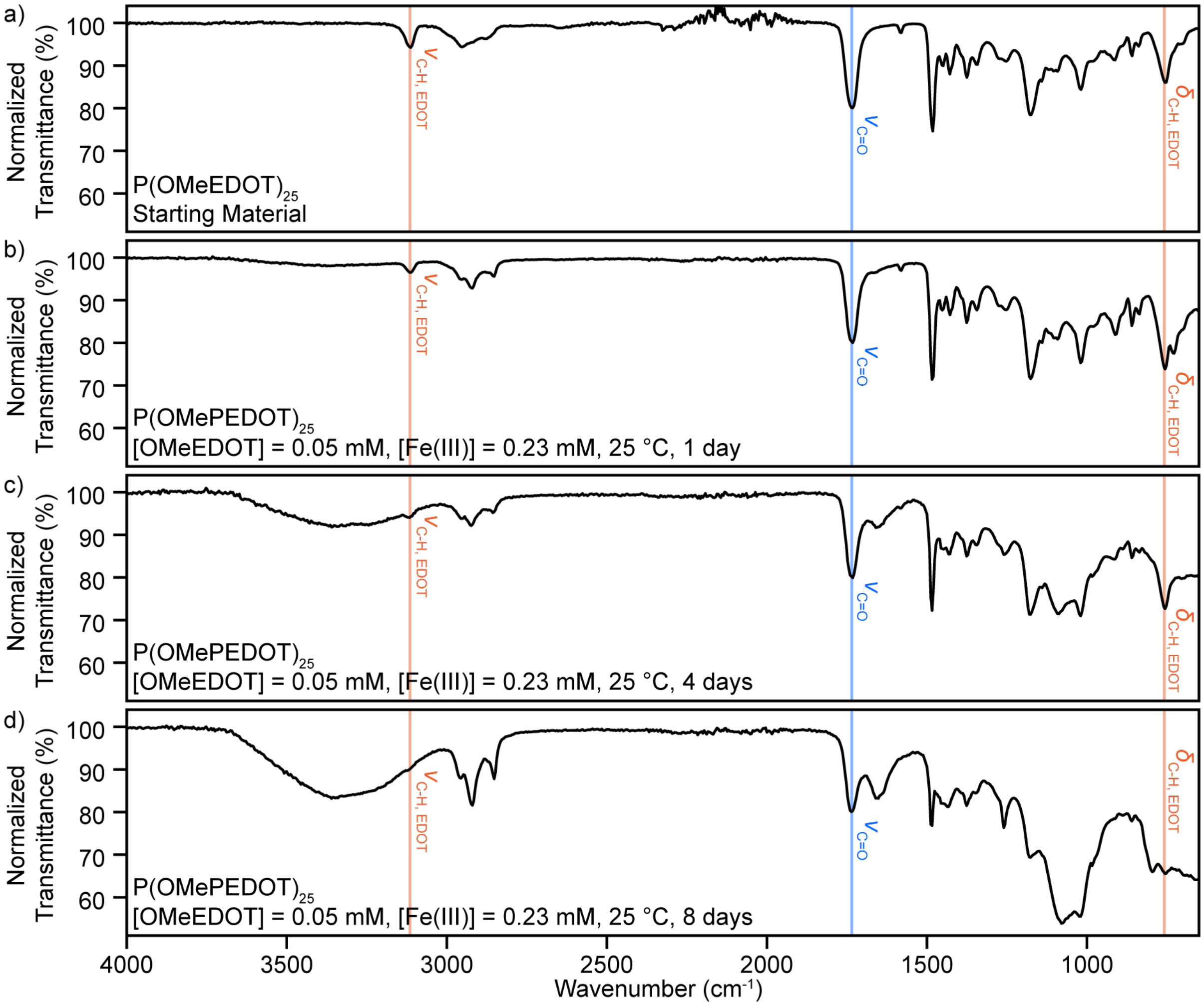


Fig. S10 Templated oxidative polymerization optimization studies. Full IR spectra after a) 0 days, b) 1 day, c) 4 days, and d) 8 days of P(OMeEDOT)$_{25}$ oxidative treatment under ambient temperature (25 °C) and stoichiometric oxidant concentration ([Fe(III)] = 0.23 mM). IR spectra are normalized to ester carbonyl absorptions bands ($\nu_{C=O}$ ~ 1730 cm^{-1}, 80% transmittance).

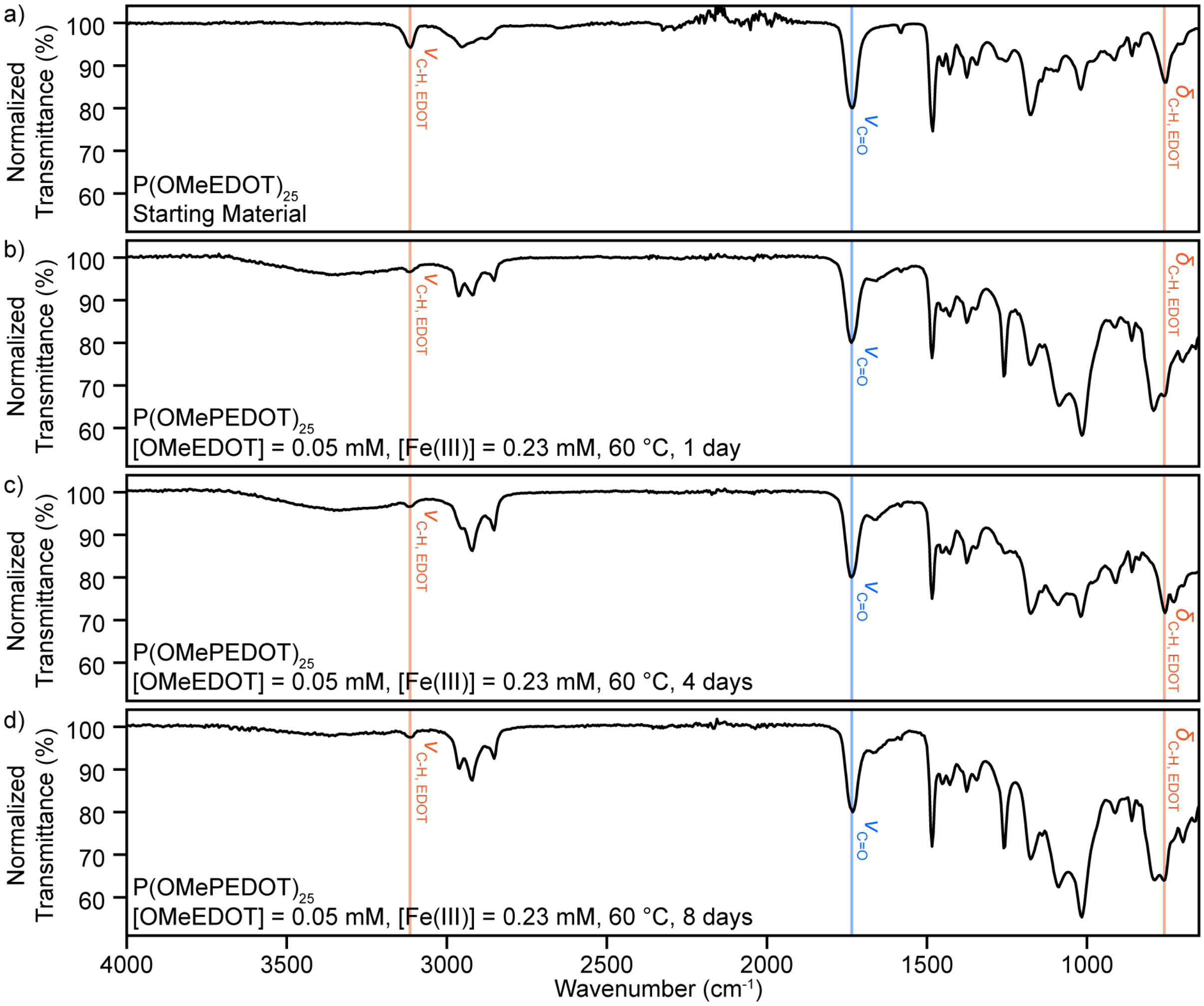


Fig. S11 Templated oxidative polymerization optimization studies. Full IR spectra after a) 0 days, b) 1 day, c) 4 days, and d) 8 days of P(OMeEDOT)$_{25}$ oxidative treatment under elevated temperature (60 °C) and stoichiometric oxidant concentration ([Fe(III)] = 0.23 mM). IR spectra are normalized to ester carbonyl absorptions bands ($\nu_{C=O}$ ~ 1730 cm^{-1}, 80% transmittance).

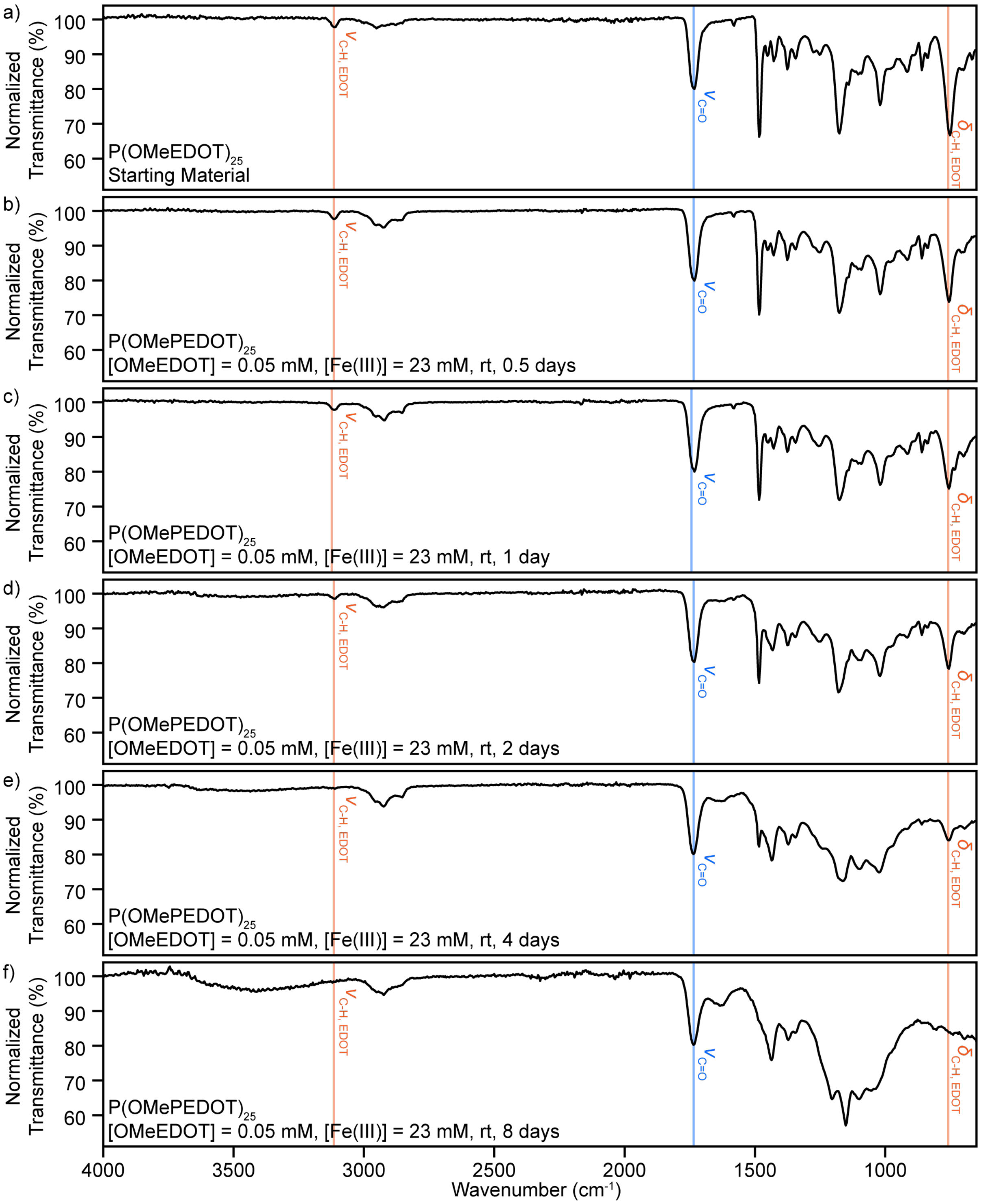


Fig. S12 Templated oxidative polymerization optimization studies. Full IR spectra after a) 0 days, b) 0.5 days, c) 1 day, d) 2 days, c) 4 days, and d) 8 days of P(OMeEDOT)$_{25}$ oxidative treatment under ambient temperature (rt ~18 – 24 °C) and excess oxidant concentration ([Fe(III)] = 23 mM). IR spectra are normalized to ester carbonyl absorptions bands ($\nu_{C=O}$ ~ 1730 cm^{-1}, 80% transmittance).

2.3.3. Control Studies

Table S3. Summary of oxidative coupling control studies for P(OMeEDOT) template polymers and hydroxymethyl EDOT monomers.

No.	P(OMeEDOT) or HOMeEDOT Starting Material	Oxidative Coupling Reaction Conditions					Oxidative Coupling Product		
		[OMeEDOT] or [HOMeEDOT][a] (mM)		[Fe(III)][a] (mM)		T	t (days)	Crude Mixture Appearance	$CHCl_3$ Solubility[b]	% yield[c]
1	P(OMeEDOT)$_{25}$ Table S1, No. 3	0.5	(0.05)	23	(23)	rt[d]	8	Green, blue and yellow solid	Insoluble	14
2		5	(5)	23	(24)		8	Blue, blue solid	Insoluble	77
3	hydroxymethyl EDOT	0.5	(0.05)	23	(23)	rt[d]	8	Green-tinted yellow solution	Partially soluble	123
4		5	(5)	23	(23)		8	Blue, blue solid	Insoluble	130

[a] Approximate values. Experimental molar ratios are provided in parentheses.

[b] Very soluble: > 10 mg/mL; partially soluble: some solvation for ~ 0.01 mg/mL; insoluble: no significant solvation at any concentration.

[c] Experimental yields greater than 100% are attributed to residual water.

[d] Experiments conducted at room temperature (approx. 18 – 24 °C).

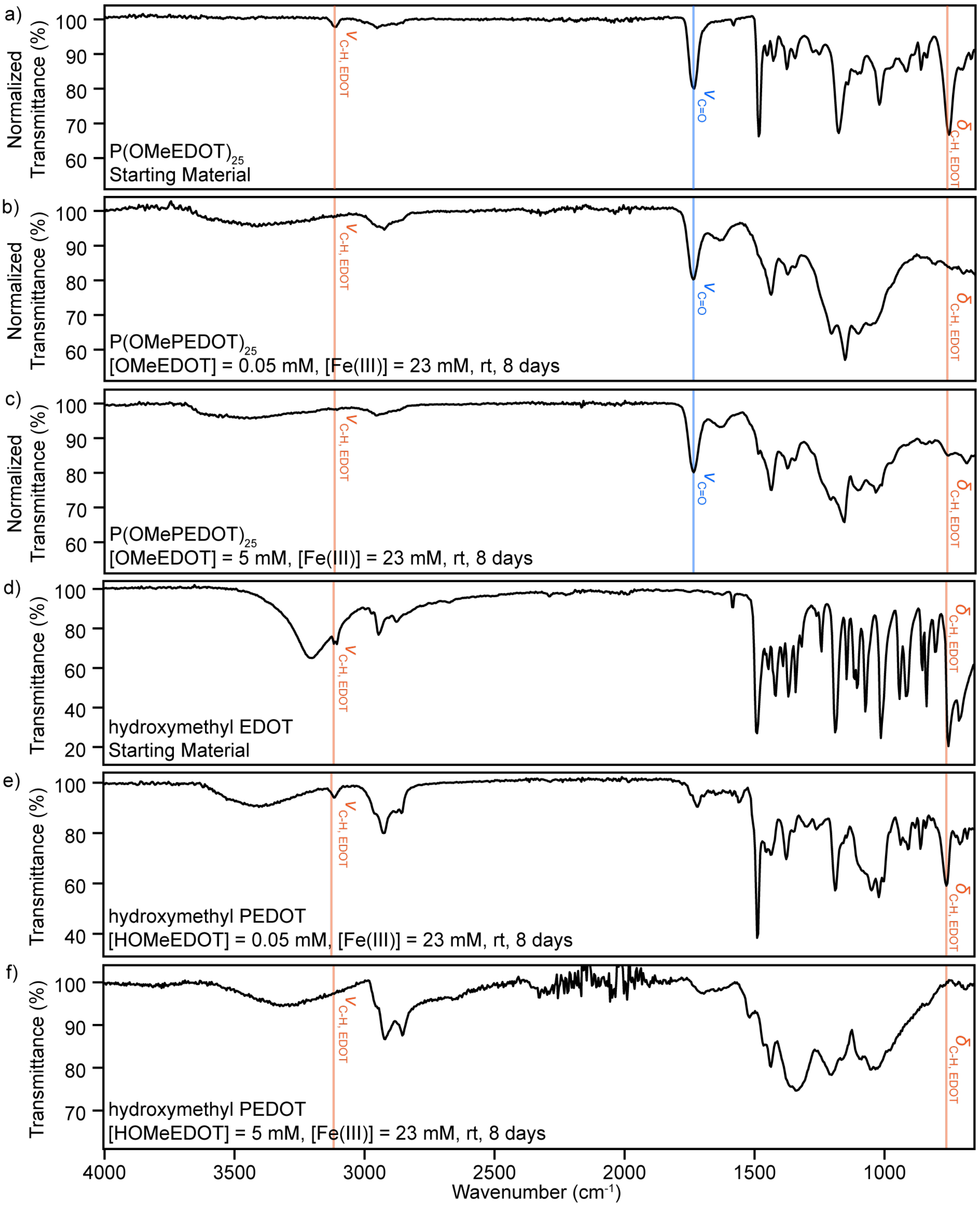
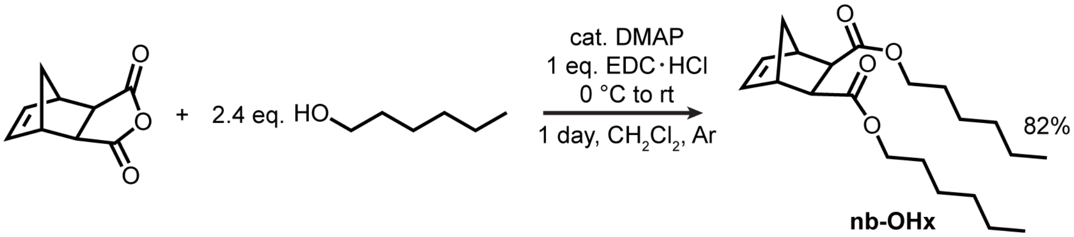


Fig. S13 Templated oxidative polymerization control studies. Full IR spectra of P(OMeEDOT) and hydroxymethyl EDOT starting materials (a and d, respectively) and products after oxidative treatment under ultradilute (b and e, respectively) and moderate (c and f, respectively) monomer unit concentrations for 8 days. Room temperature (rt) is approximately 18 – 24 °C.

3. P(OMePEDOT-*b*-OHx) Block Copolymers

3.1. nb-OHx Monomer



Scheme S2. nb-OHx synthesis.

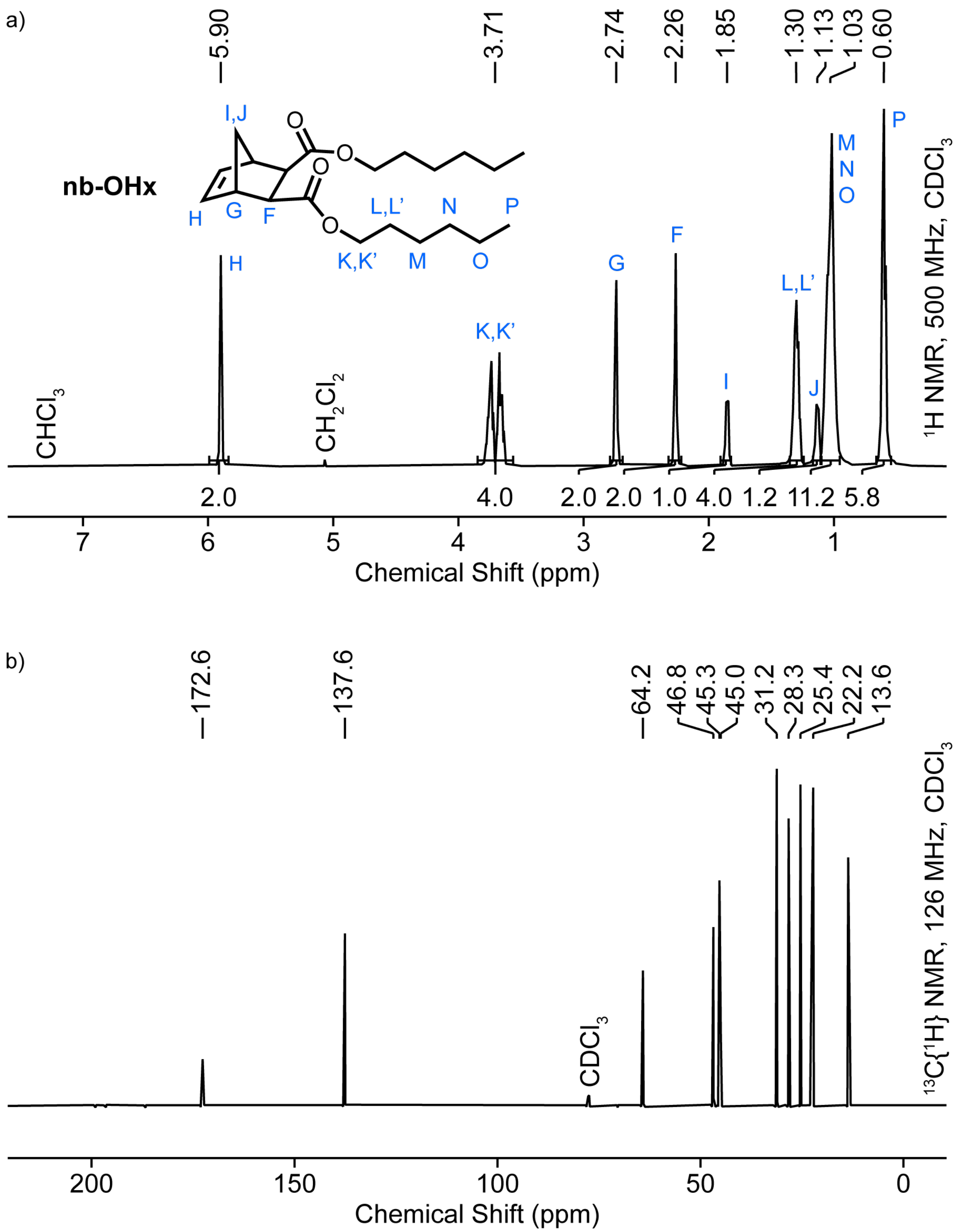


Fig. S14 a) ^{1}H NMR and b) ^{13}C{^{1}H} NMR (CDCl$_3$, rt) spectra of nb-OHx.

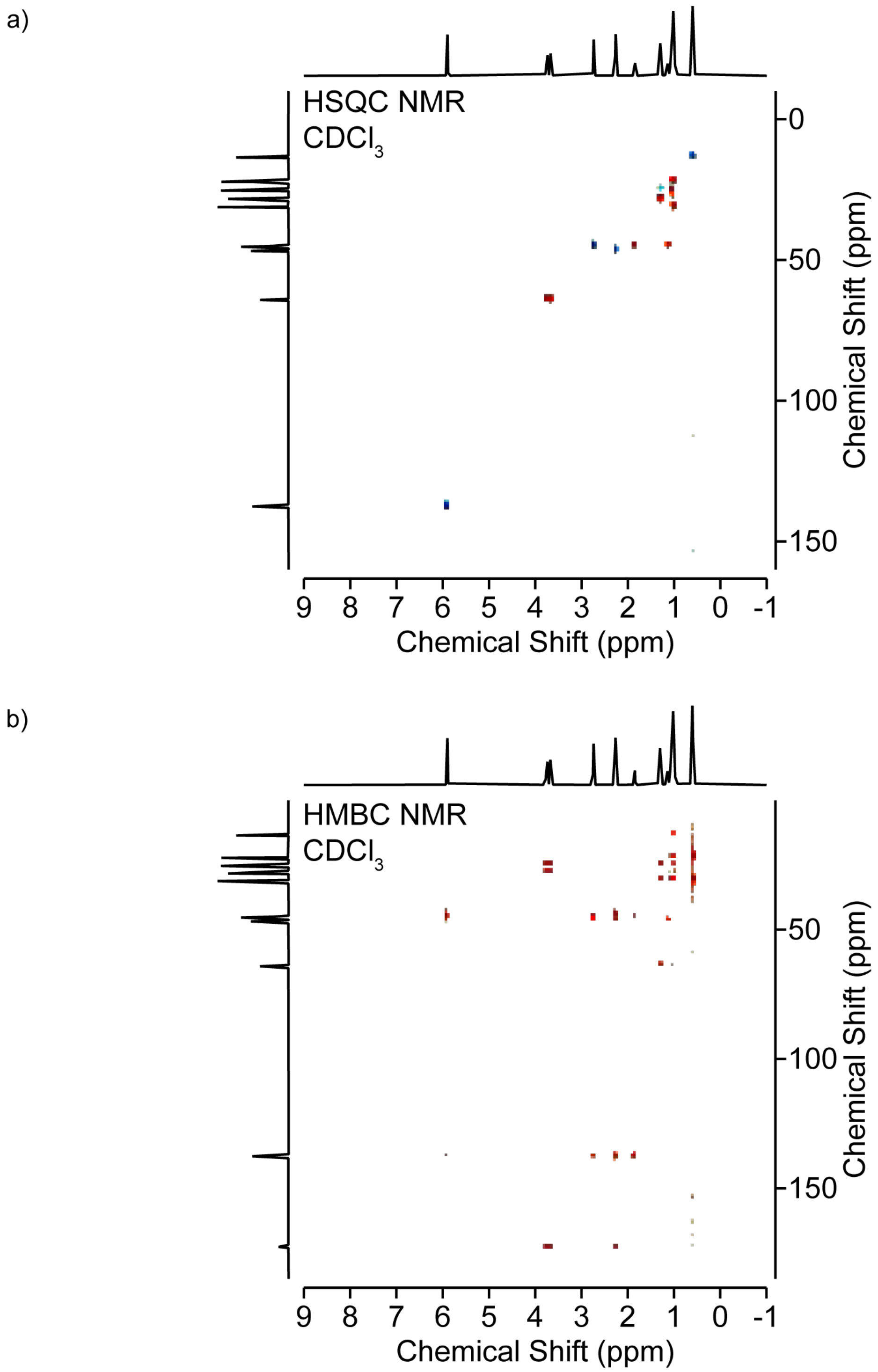


Fig. S15 a) HSQC and b) HMBC NMR ($CDCl_3$, rt) spectra of nb-OHx.

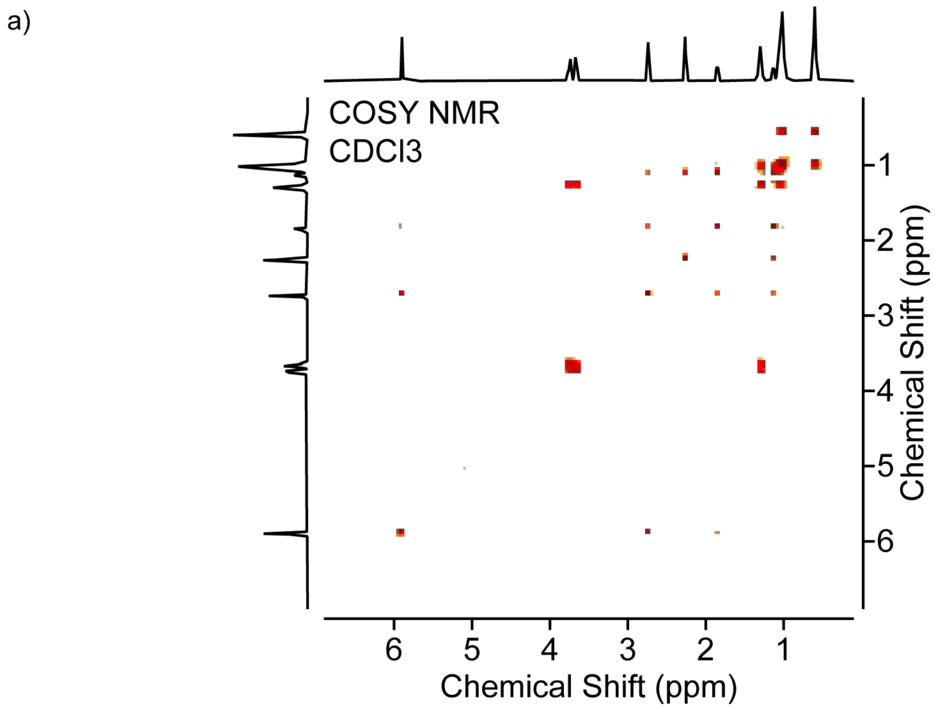


Fig. S16 COSY NMR ($CDCl_3$, rt) spectrum of nb-OHx.

3.2. P(OMeEDOT-*b*-OHx) Block Copolymers

Table S4. Summary of P(OMeEDOT-*b*-OHx) reaction conditions and properties.

No.	Polymer	[nb-OMeEDOT]:[nb-OHx]:[cat.][a]		block ratio[b]		$M_{n,\ GPC}$ (kg/mol)	$Đ_{GPC}$	% yield[c]
				OMeEDOT	OHx			
1	P(OMeEDOT$_{25}$-*b*-OHx$_{25}$)	25:25:1	(26:26:1)	1.0	1.3	19.2[d]	1.17[d]	88
2	P(OMeEDOT$_{25}$-*b*-OHx$_{0}$)	25:0:1	(24:0:1)	1.0	0	13.2[e]	1.12[e]	62
3	P(OMeEDOT$_{25}$-*b*-OHx$_{5}$)	25:5:1	(24:5:1)	1.0	0.3	16.3[e]	1.14[e]	110
4	P(OMeEDOT$_{25}$-*b*-OHx$_{15}$)	25:15:1	(24:15:1)	1.0	0.8	20.5[e]	1.18[e]	97
5	P(OMeEDOT$_{25}$-*b*-OHx$_{25}$)	25:25:1	(24:24:1)	1.0	1.2	25.2[e]	1.17[e]	95
6	P(OMeEDOT$_{25}$-*b*-OHx$_{50}$)	25:50:1	(24:49:1)	1.0	2.4	35.5[e]	1.22[e]	101

[a] Approximate values. Experimental molar ratios are provided in parentheses.
[b] Calculated from ^{1}H NMR spectra ($CDCl_3$, rt). For sample calculation see **Figure S21**.
[c] Experimental yields greater than 100% are attributed to residual methanol.
[d] $CHCl_3$ GPC measured at 40 °C, calibrated against polystyrene standards.
[e] THF GPC measured at 40 °C, calibrated against polystyrene standards.

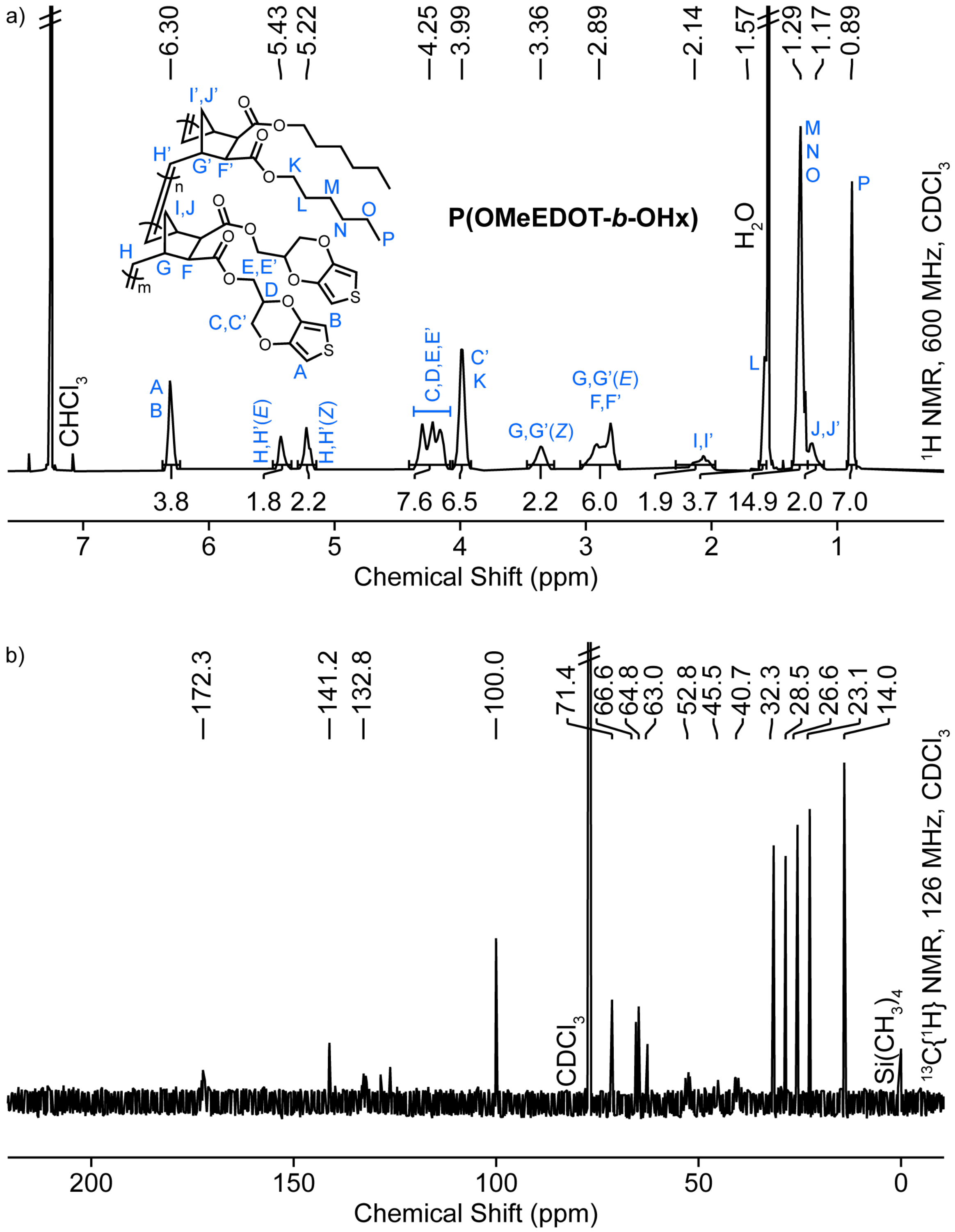


Fig. S17 Representative a) ^{1}H and b) ^{13}C{^{1}H} NMR ($CDCl_3$, rt) spectra of P(OMeEDOT$_{25}$-*b*-OHx$_{25}$), featuring a mixture of *E* (45%) and *Z* (55%) olefins.

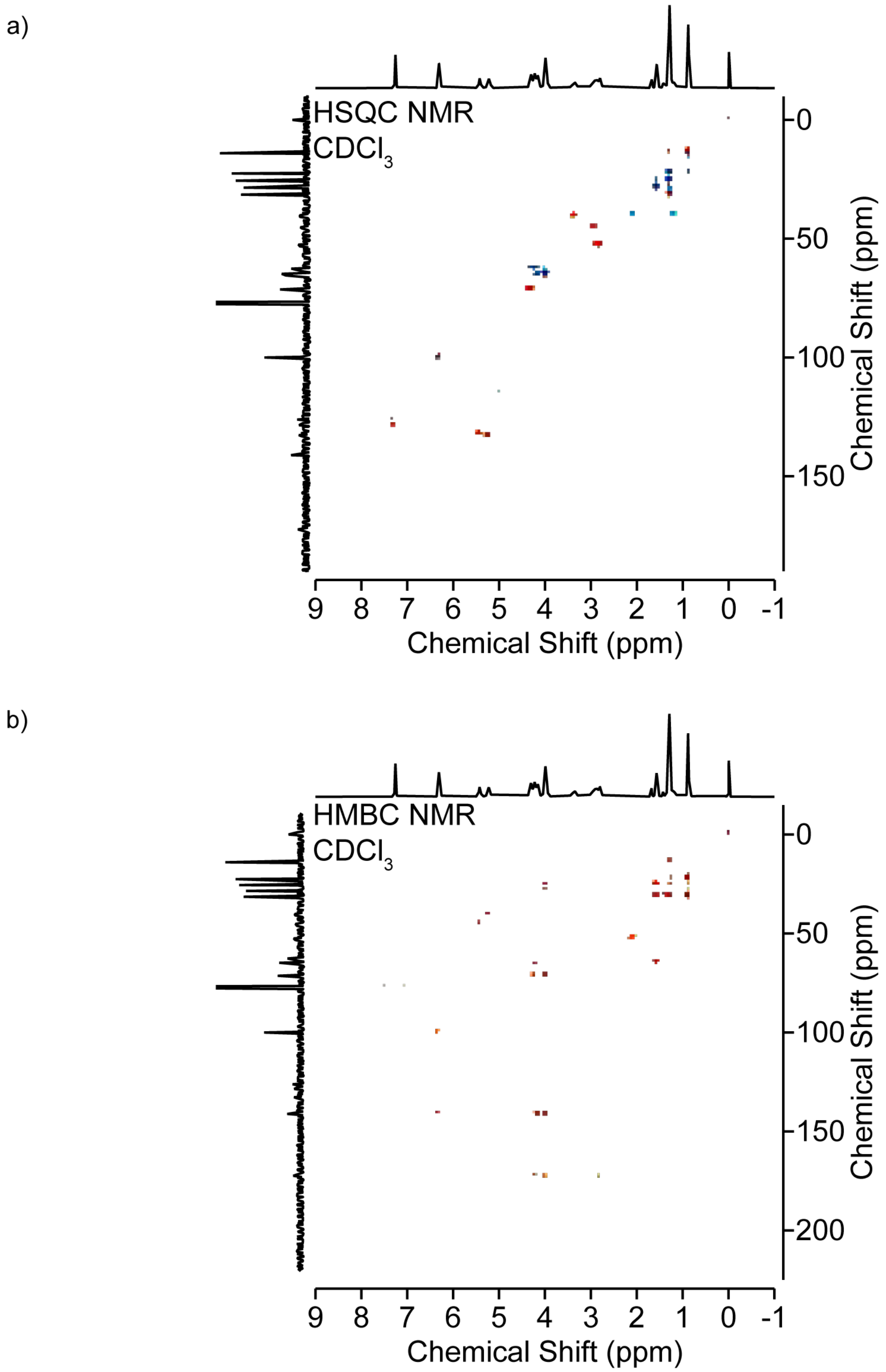


Fig. S18 Representative a) HSQC and b) HMBC NMR ($CDCl_3$, rt) spectra of P(OMeEDOT$_{25}$-*b*-OHx$_{25}$).

a)

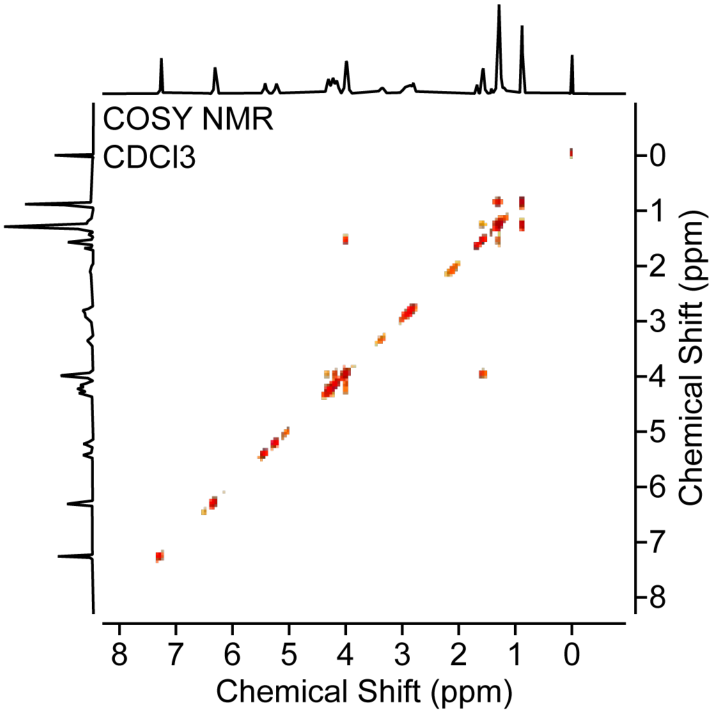


Fig. S19 Representative COSY NMR ($CDCl_3$, rt) spectrum of P(OMeEDOT$_{25}$-*b*-OHx$_{25}$).

3.3. P(OMePEDOT-*b*-OHx) Block Copolymers

3.3.1. Sample Calculations and Analysis

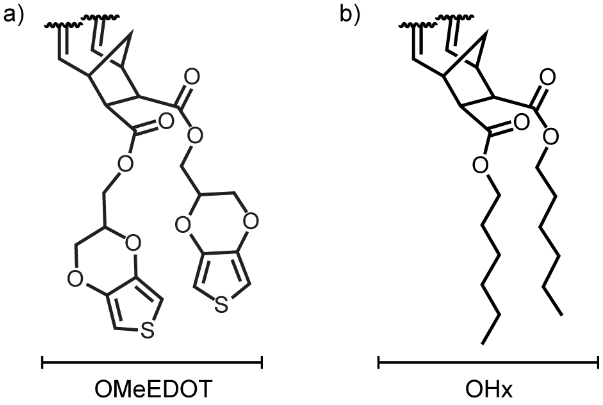
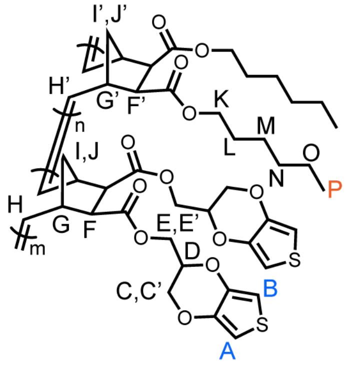


Fig. S20 Monomer unit definitions, a) OMeEDOT and b) OHx, for P(OMeEDOT-*b*-OHx).

a)



b) Ratio of OMeEDOT to OHx Blocks

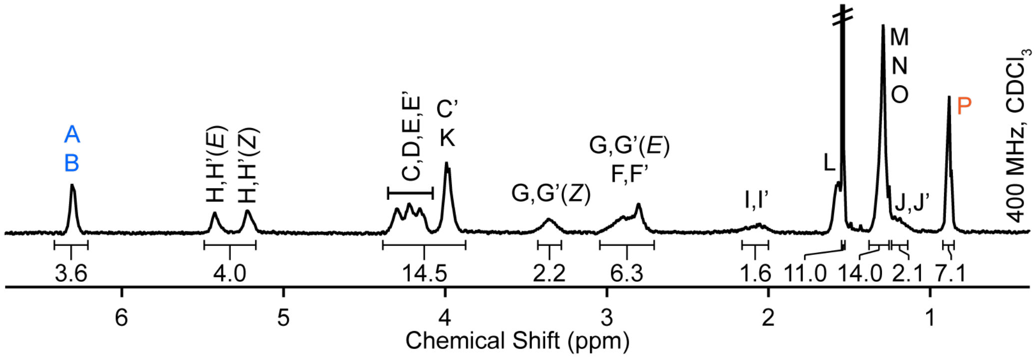
$$\frac{n_{\text{OMeEDOT}}}{n_{\text{OHx}}} = \frac{H_{\text{A,B, NMR}}/H_{\text{A,B, relative}}}{H_{\text{P, NMR}}/H_{\text{P, relative}}} = \frac{H_{\text{A,B, NMR}}/4}{H_{\text{P, NMR}}/6} = \frac{1.0}{1.3}$$

c) Mole fraction of OMeEDOT and OHx Blocks

$$x_{\text{OMeEDOT}} = \frac{n_{\text{OMeEDOT}}}{n_{\text{OMeEDOT}} + n_{\text{OHx}}} = \frac{1.0}{1.0 + 1.3} = 0.44$$

$$x_{\text{OHx}} = \frac{n_{\text{OHx}}}{n_{\text{OMeEDOT}} + n_{\text{OHx}}} = \frac{1.3}{1.0 + 1.3} = 0.56$$

d)



e) Average Monomer Unit Weight

$$M_{\text{o, ave}} = (x_{\text{OMeEDOT}} \cdot M_{\text{o, OMePEDOT}}) + (x_{\text{OHx}} \cdot M_{\text{o, OHx}}) = 410 \text{ Da}$$

f) Number Average Degree of Polymerization

$$X_{\text{n}} = \frac{M_{\text{n}}}{M_{\text{o, ave}}} = 39$$

$$X_{\text{n, OMeEDOT}} = X_{\text{n}} \cdot x_{\text{OMeEDOT}} = 17$$

$$X_{\text{n, OHx}} = X_{\text{n}} \cdot x_{\text{OHx}} = 22$$

g) Approximate Contour Length

$$L \approx X_{\text{n, OMeEDOT}} \cdot d_{\text{OMePEDOT}} + X_{\text{n, OHx}} \cdot d_{\text{OHx}} \approx 270 \text{ Å} \approx 27 \text{ nm}$$

h)

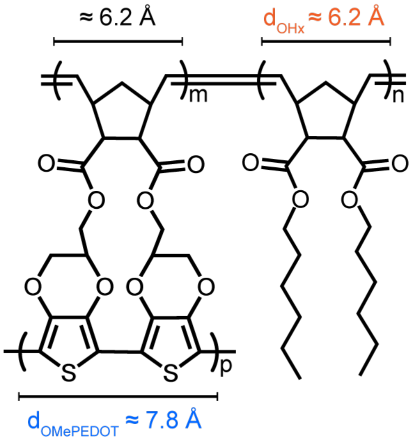


Fig. S21 Sample calculations for P(OMeEDOT-*b*-OHx) and P(OMePEDOT-*b*-OHx) block copolymers. a) P(OMeEDOT-*b*-OHx) proton labels for ^{1}H NMR analysis. Sample calculations for b) OMeEDOT:OHx block ratios and c) OMeEDOT and OHx block mole fractions from d) ^{1}H NMR spectra. Sample calculations for e) average monomer unit weight and f) number average degree of polymerization used to calculate g) approximate contour length. h) Approximate OMePEDOT and OHx monomer unit lengths from the literature.[7,8]

3.3.2. Synthesis and Characterization

Table S5. Summary of P(OMePEDOT-*b*-OHx) starting materials, reaction conditions, and properties.

No.	P(OMeEDOT-*b*-OHx)	Oxidative Coupling Reaction Conditions				P(OMePEDOT-*b*-OHx) Oxidative Coupling Product				
	Starting Material	[OMeEDOT][a] (mM)	[Fe(III)][a] (mM)	T (°C)	t (days)	Crude Mixture Appearance	$CHCl_3$ Solubility[b]	$M_{n,\ GPC}$ (kg/mol)	$Đ_{GPC}$	% yield[c]
1	P(OMeEDOT$_{25}$-*b*-OHx$_{25}$) Table S4, No. 1	0.05 (0.05)	23 (27)	rt[d]	4	Dark green, yellow solid	Very soluble	16.1[e]	1.24[e]	62
2		0.05 (0.05)	23 (27)	rt[d]	8	Dark green, yellow solid	Very soluble	16.4[e]	1.11[e]	56
3	P(OMeEDOT$_{25}$-*b*-OHx$_{0}$) Table S4, No. 2	0.05 (0.05)	23 (24)	rt[d]	4	Green-tinted yellow, blue and yellow solid	Insoluble	N/A	N/A	149
4	P(OMeEDOT$_{25}$-*b*-OHx$_{5}$) Table S4, No. 3	0.05 (0.05)	23 (24)	rt[d]	4	Dark green, yellow solid	Insoluble	N/A	N/A	105
5	P(OMeEDOT$_{25}$-*b*-OHx$_{15}$) Table S4, No. 4	0.05 (0.05)	23 (23)	rt[d]	4	Dark green, yellow solid	Partially soluble	15.7[f]	1.20[f]	44
6	P(OMeEDOT$_{25}$-*b*-OHx$_{25}$) Table S4, No. 5	0.05 (0.05)	23 (23)	rt[d]	4	Dark green, yellow solid	Very soluble	20.3[f]	1.22[f]	41
7	P(OMeEDOT$_{25}$-*b*-OHx$_{50}$) Table S4, No. 6	0.05 (0.05)	23 (23)	rt[d]	4	Dark green, yellow solid	Very soluble	31.8, 311.9[f]	1.25, 1.33[f]	56

[a] Approximate values. Experimental molar ratios are provided in parentheses. Monomer unit, OMeEDOT, defined in **Fig. S20**.

[b] Very soluble: > 10 mg/mL; partially soluble: some solvation for ~ 0.01 mg/mL; insoluble: no significant solvation at any concentration.

[c] Experimental yields greater than 100% are attributed to residual water.

[d] Experiments conducted at room temperature (approx. 18 – 24 °C).

[e] $CHCl_3$ GPC measured at 40 °C, calibrated against polystyrene standards.

[f] THF GPC measured at 40 °C of reduced polymers, calibrated against polystyrene standards.

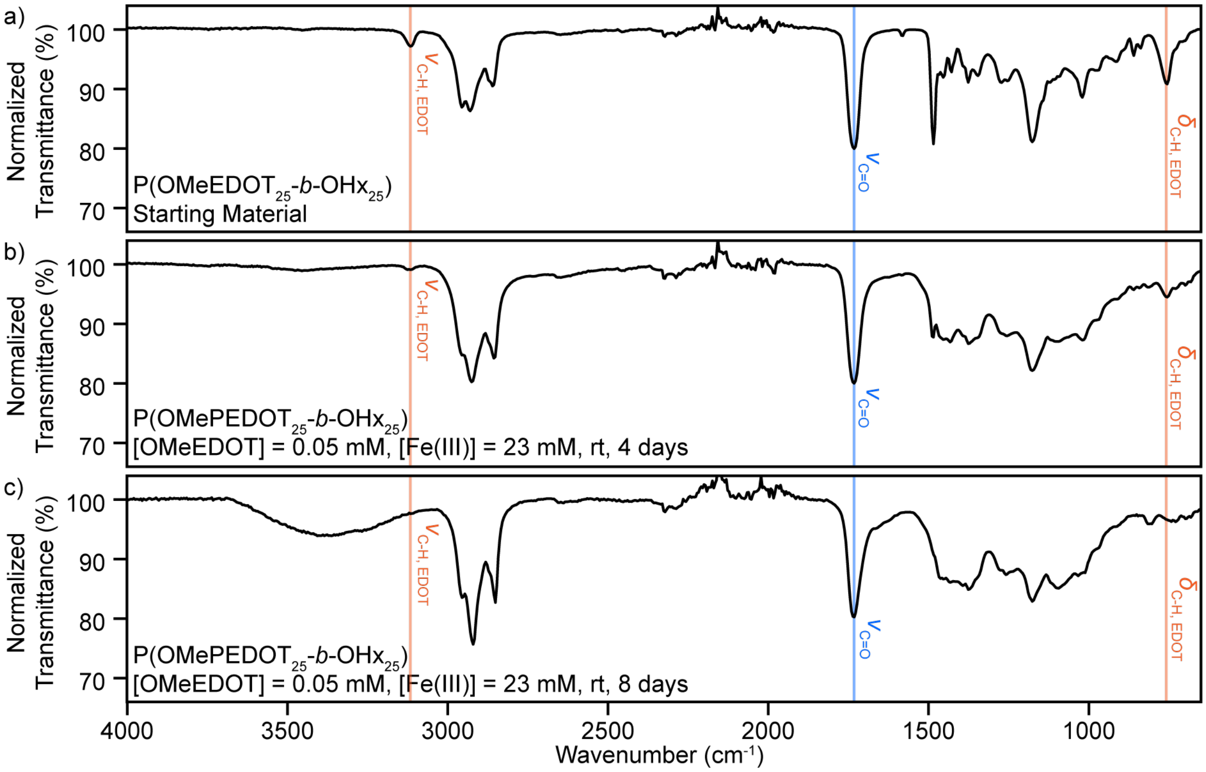
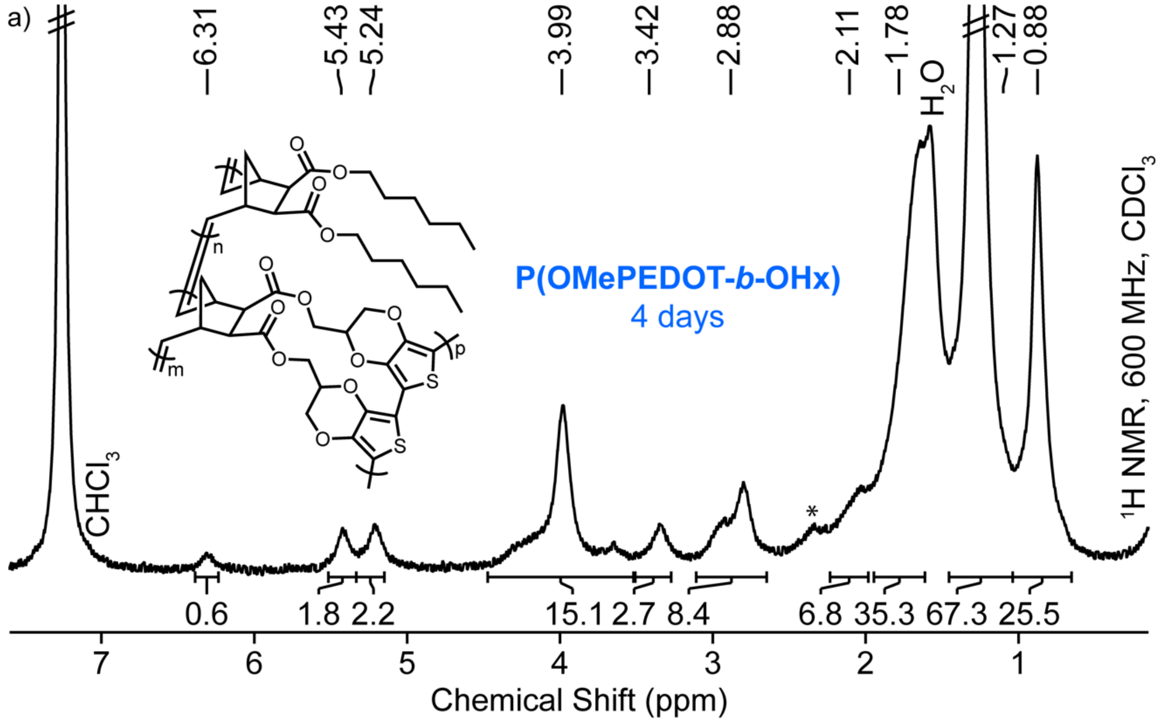


Fig. S22 Full IR spectra of a) P(OMeEDOT$_{25}$-*b*-OHx$_{25}$) and P(OMePEDOT$_{25}$-*b*-OHx$_{25}$) after b) 4 and c) 8 days of oxidative treatment. IR spectra are normalized to ester carbonyl absorptions bands ($\nu_{C=O}$ ~ 1730 cm^{-1}, 80% transmittance). Room temperature (rt) is approximately 18 – 24 °C.



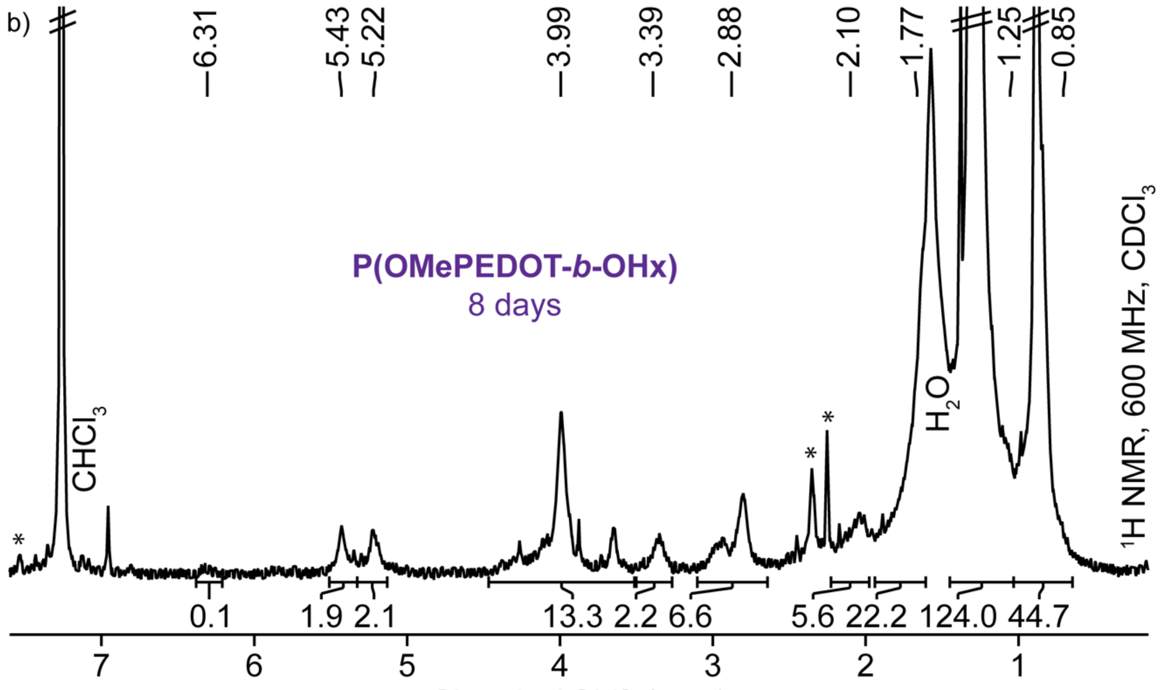


Fig. S23 ^{1}H NMR ($CDCl_3$, rt) spectra of P(OMePEDOT$_{25}$-*b*-OHx$_{25}$) after a) 4 and b) 8 days of oxidative treatment. * = impurities.

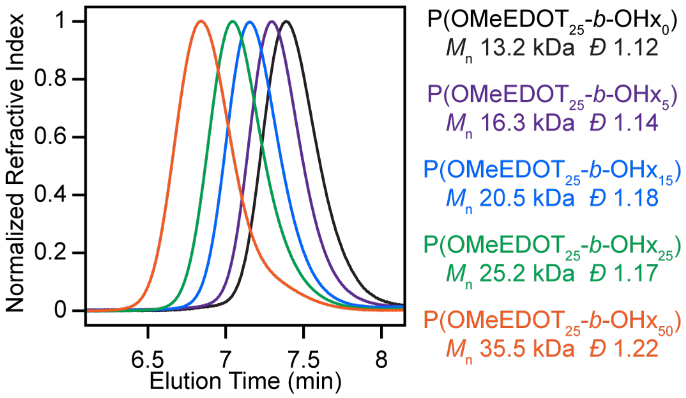


Fig. S24 GPC traces (THF, 40 °C) of P(OMeEDOT-*b*-OHx) template polymers. P(OMeEDOT$_{25}$-*b*-OHx$_0$, P(OMeEDOT$_{25}$-*b*-OHx$_5$), P(OMeEDOT$_{25}$-*b*-OHx$_{15}$), P(OMeEDOT$_{25}$-*b*-OHx$_{25}$) and P(OMeEDOT$_{25}$-*b*-OHx$_{50}$) were synthesized through ROMP using [nb-OMeEDOT]:[nb-OHx]:[catalyst] = 25:0:1, 25:5:1, 25:15:1, 25:25:1, and 25:50:1, respectively.

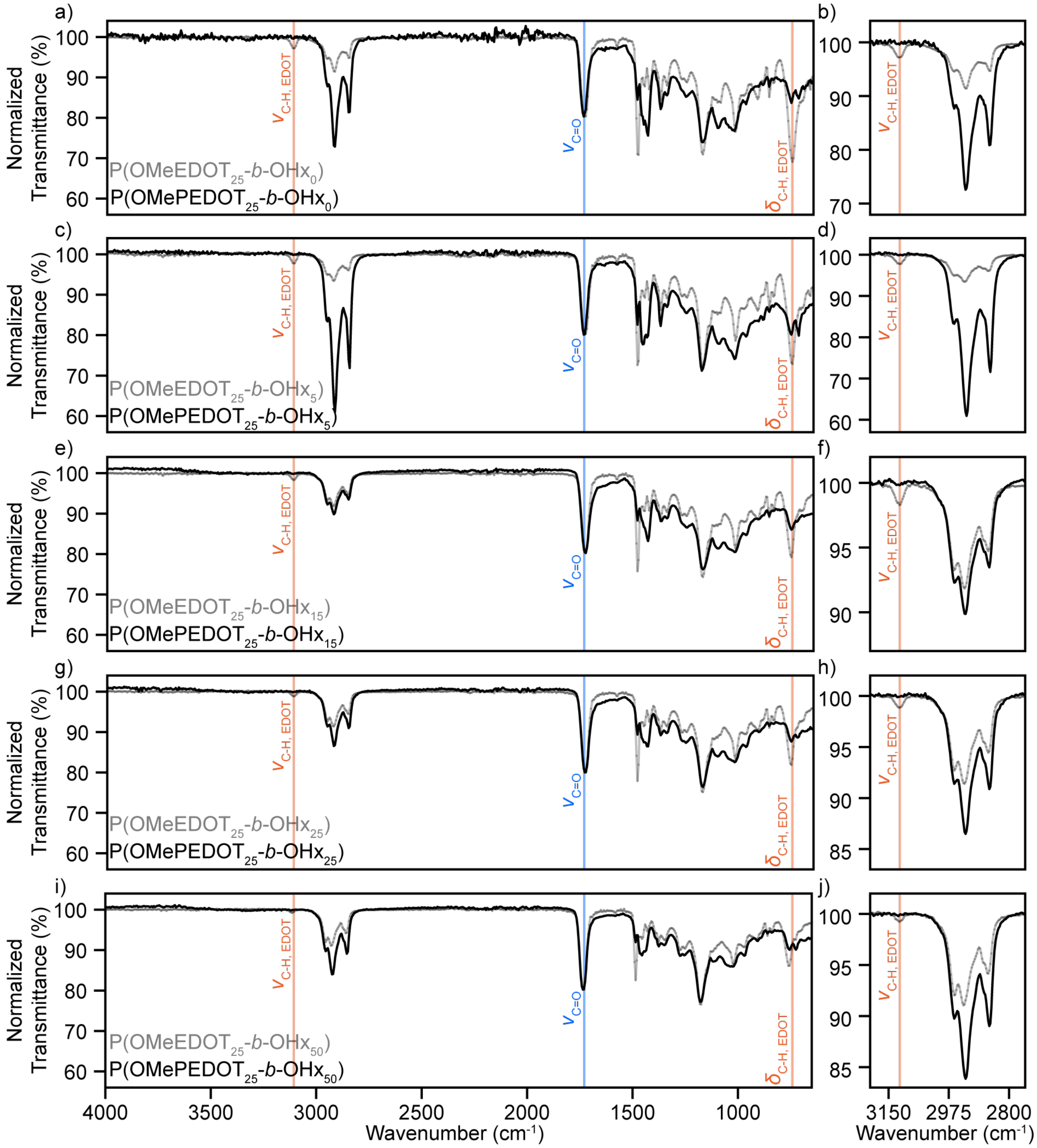


Fig. S25 (left) Full IR spectra and (right) C–H stretch region of IR spectra of P(OMeEDOT-*b*-OHx) (grey) and P(OMePEDOT-*b*-OHx) after 4 days of oxidative treatment (black) for polymers with varying redox-active to aliphatic block ratios.

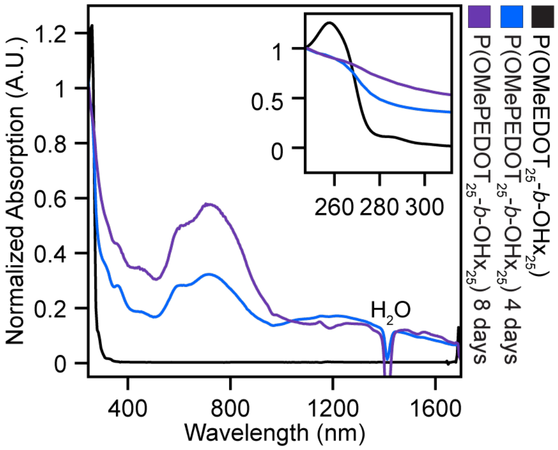


Fig. S26 Optical absorption spectra of P(OMeEDOT$_{25}$-*b*-OHx$_{25}$) and P(OMePEDOT$_{25}$-*b*-OHx$_{25}$) after 4 and 8 days of oxidative treatment.

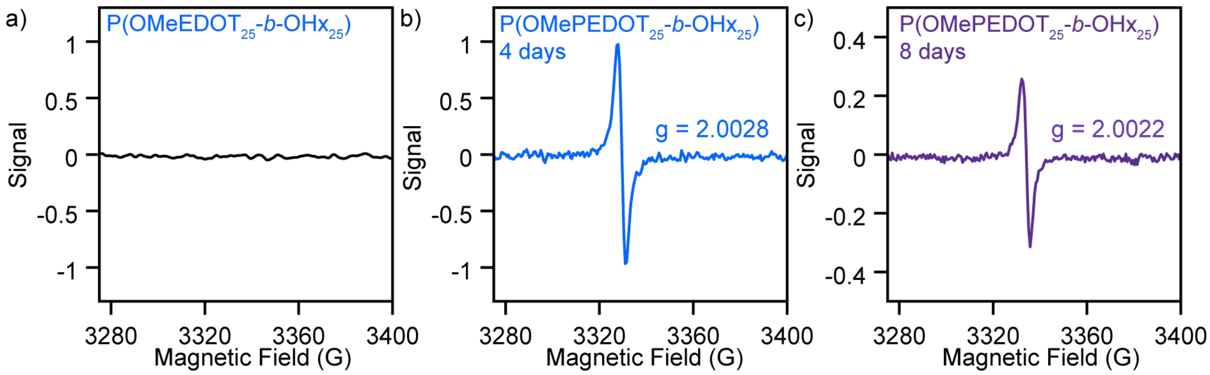


Fig. S27 Electron paramagnetic resonance spectra of P(OMeEDOT$_{25}$-*b*-OHx$_{25}$) and P(OMePEDOT$_{25}$-*b*-OHx$_{25}$) after 4 and 8 days of oxidative treatment.

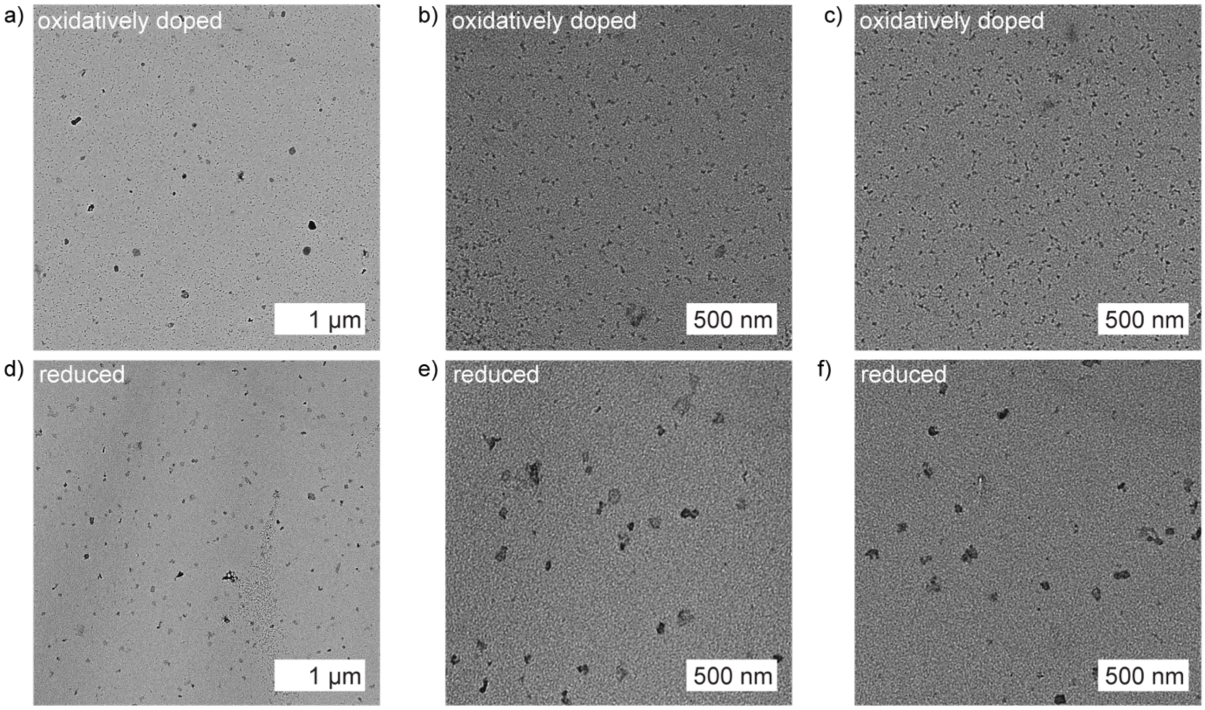


Fig. S28 TEM images at different magnifications of a – c) as-prepared (oxidatively doped) and d – f) reduced P(OMePEDOT$_{25}$-*b*-OHx$_{25}$) polymers drop-cast from chloroform solution.

4. Computational Modeling of Template Dimers

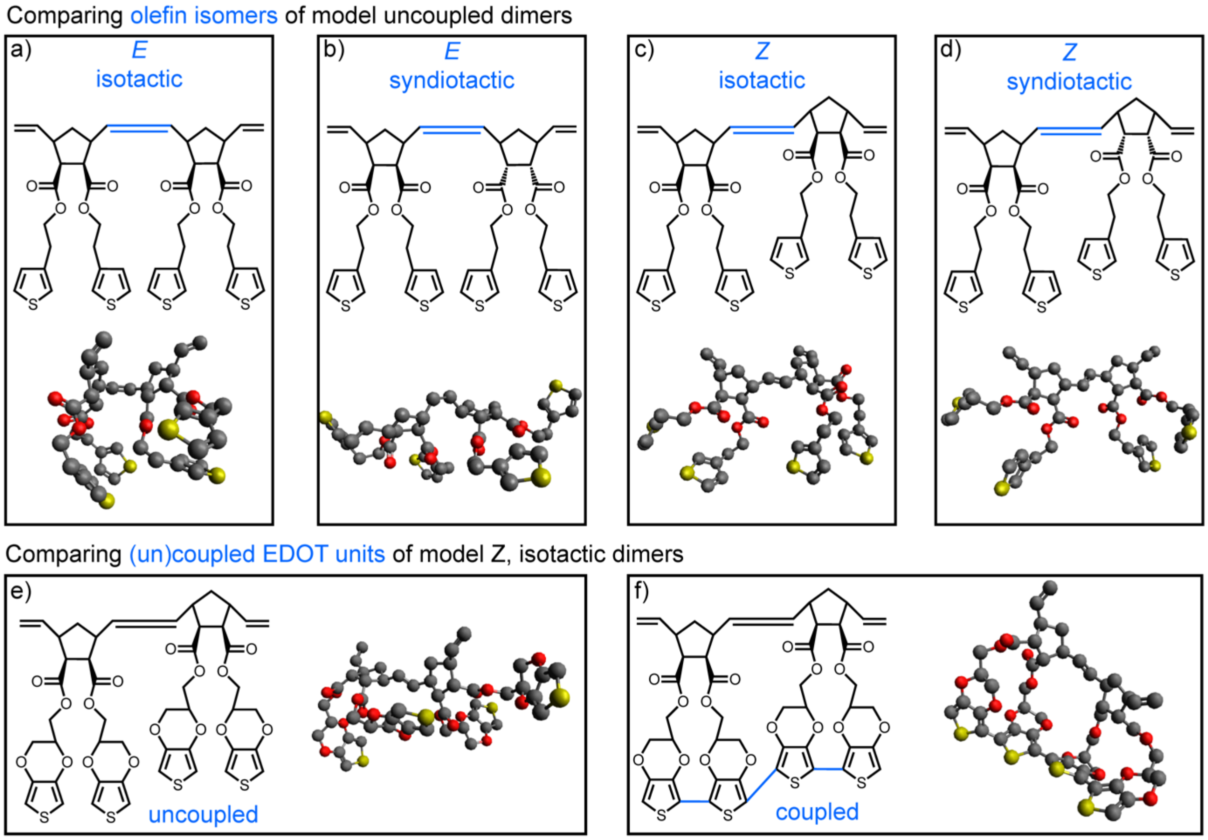


Fig. 29 Preliminary computational modeling studies of template dimers, featuring chemical structures and DFT-optimized geometry optimizations (B3LYP functional, 6-31G(d) basis set). Model dimers containing 3-ethylthiophene pendant units featuring a) *E* isotactic, b) *E* syndiotactic, c) *Z* isotactic, and d) *Z* syndiotactic olefin isomers were compared and found to exhibit similar optimized geometries. Then, model dimers containing *Z* isotactic olefins and featuring e) uncoupled and f) coupled EDOT units were compared. Pendant EDOT units are able to get close enough to couple without causing distortions in the optimized geometries, likely due to template free rotation and flexibility. Hydrogen atoms have been omitted for clarity.

5. References

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