Structure–Property Relationship of Ester-Functionalized and Hydrolyzed ProDOT Polymers for Electrochromic Applications

Alina Tilekkabylova[a], Sanzhar Abish[b], Adil Zulkarnayev[a], Dana Kanzhigitova[c,*], Mirat Karibayev[c], Salimgerey Adilov[b]

[a]Department of Chemical and Materials Engineering, Nazarbayev University, Astana, 010000, Kazakhstan
[b]Department of Chemistry, School of Sciences and Humanities, Nazarbayev University, Astana, 010000, Kazakhstan
[c]Renewable Energy Lab, National Laboratory Astana, Astana, 010000, Kazakhstan.
[*]Corresponding author: dana.kanzhigitova@nu.edu.kz

Materials

3,4-Dimethoxythiophene, 2,2-bis(bromomethyl)propane-1,3-diol, p-toluenesulfonic acid (p-TSA), 2-ethylhexanoic acid, N-bromosuccinimide (NBS), palladium(II) acetate [$Pd(OAc)_2$], pivalic acid, potassium carbonate (K_2CO_3), magnesium sulfate ($MgSO_4$), sodium bicarbonate ($NaHCO_3$), and all organic solvents were purchased from Sigma-Aldrich and used as received unless otherwise stated. Dry toluene and dry N,N-dimethylacetamide (DMAc) were used for moisture-sensitive synthesis steps. Hexane, dichloromethane, ethyl acetate, diethyl ether, methanol, acetone, and chloroform were used for extraction, precipitation, column chromatography, Soxhlet purification, and polymer recovery. Deionized water was used for all aqueous washing procedures.

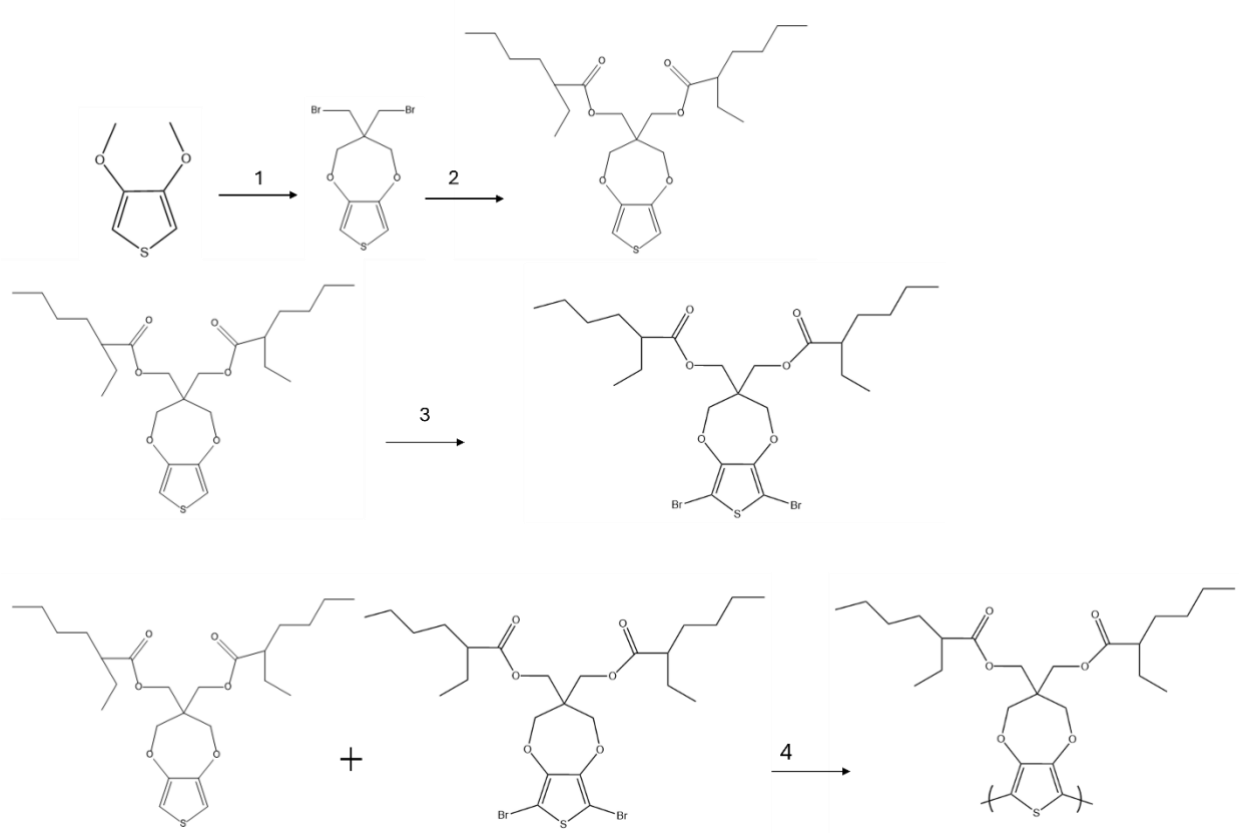

Figure S1. Synthesis procedure of the monomer and its polymerization

Synthesis of 3,3-bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (1)

Monomer and polymer was prepared according to a previously reported procedure with minor modification[1], [2], [3]. In brief, 3,4-dimethoxythiophene (1.00 g, 6.94 mmol), 2,2-bis(bromomethyl)propane-1,3-diol (3.72 g, 14.2 mmol), and p-toluenesulfonic acid (p-TSA, 0.119 g, 0.694 mmol) were combined in dry toluene under an argon atmosphere. The reaction mixture was heated under reflux to promote the acid-catalyzed transacetalization/cyclization reaction. After the initial reaction period, an additional portion of 2,2-bis(bromomethyl)propane-1,3-diol (0.372 g, 1.42 mmol) was introduced, and the reaction was continued until completion. The mixture was then cooled to room temperature and worked up by extraction with ethyl acetate and water. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude dark residue was purified by silica gel column chromatography using a 1:1 hexanes/dichloromethane eluent to afford M4 as a pale-yellow solid.

Synthesis of ProDOT bis(2-ethylhexanoate) derivative (2)

ProDOT(CH_2Br)$_2$ (1.00 g, 2.92 mmol, 1.0 equiv.), 2-ethylhexanoic acid (ca. 1.1 g, 7.6 mmol, 2.6 equiv.), K_2CO_3 (1.21 g, 8.76 mmol, 3.0 equiv.), and dry DMAc (ca. 28 mL) were added to a dry round-bottom flask under an argon atmosphere. The reaction mixture was heated at 100 °C overnight. After cooling to room temperature, the mixture was extracted with diethyl ether and brine. The combined organic layers were washed several times with saturated $NaHCO_3$ solution to remove residual acid, followed by washing with water. The organic phase was then dried, filtered, and concentrated under reduced pressure. The crude oily residue was purified by silica gel column chromatography, using a gradient from hexanes to 20% ethyl acetate in hexanes. After drying under high vacuum overnight, the desired product was obtained as a pale yellow oil.

Synthesis of ProDOT(EH)-Br_2 (3)

ProDOT(EH)$_2$, bearing 2-ethylhexanoate ester side chains, was brominated following a modified literature procedure. In a typical reaction, ProDOT(EH)$_2$ (1.00 g, approximately 2.13 mmol, 1.0 equiv.) was dissolved in dry DMAc (approximately 24 mL) under argon and cooled to 0 °C. NBS (0.84 g, 4.69 mmol, 2.2 equiv.) was added in one portion, and the reaction mixture was protected from light with aluminum foil. The mixture was stirred overnight while slowly warming to room temperature. The reaction mixture was then extracted with diethyl ether, washed with saturated $NaHCO_3$ solution and brine, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient from hexanes to 20% ethyl acetate in hexanes. The desired dibrominated monomer, ProDOT(EH)-Br_2, was obtained as a pale-yellow oil after drying under high vacuum.

Polymerization of ProDOT(EH)-Br_2

PProDOT(EHE) was synthesized via direct heteroarylation polymerization using equimolar amounts of ProDOT(EHE) and ProDOT(EHE)-Br_2. ProDOT(EHE) (**0.3572 g, 1.20 mmol, 1.0 equiv.**) and ProDOT(EHE)-Br_2 (**0.5461 g, 1.20 mmol, 1.0 equiv.**) were initially weighed into separate vials. $Pd(OAc)_2$ (**0.0052 g, 2 mol%**), pivalic acid (**0.0444 g, approximately 0.3 equiv.**), K_2CO_3 (**0.436 g, 2.5 equiv.**), and a magnetic stir bar were added to a 50 mL round-bottom flask. The monomers were transferred into the flask using dry DMAc (**12 mL**), and the reaction mixture was degassed by argon bubbling. The flask was then placed in an oil bath at **100 °C**, and the reaction was stirred vigorously overnight. After cooling to room temperature, the polymer was precipitated into stirred methanol. The precipitate was collected in a Soxhlet thimble and purified by sequential washing with methanol, acetone, ethyl acetate, and hexane, followed by extraction with $CHCl_3$. The chloroform fraction appeared as a dark magenta solution.

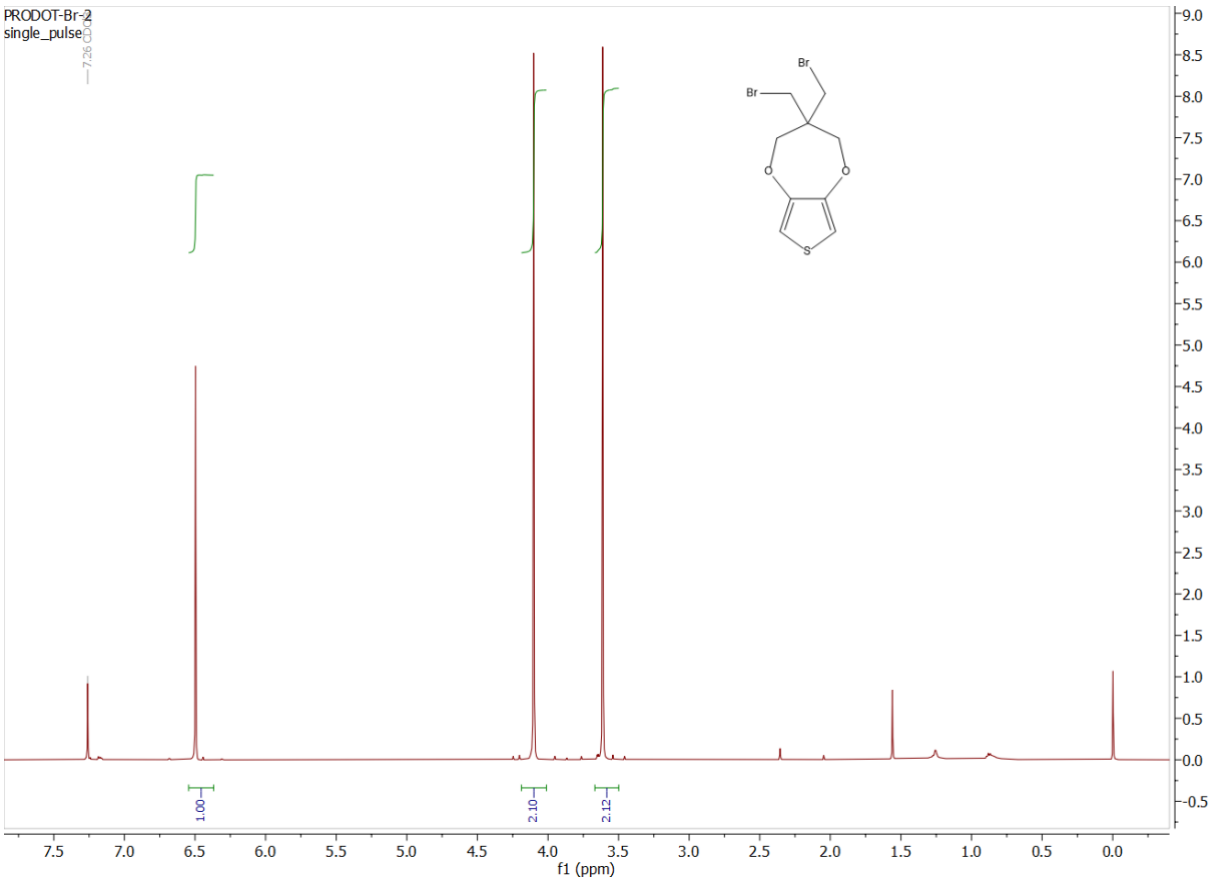

Figure S2. ^{1}H NMR spectra of 3,3-bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine.

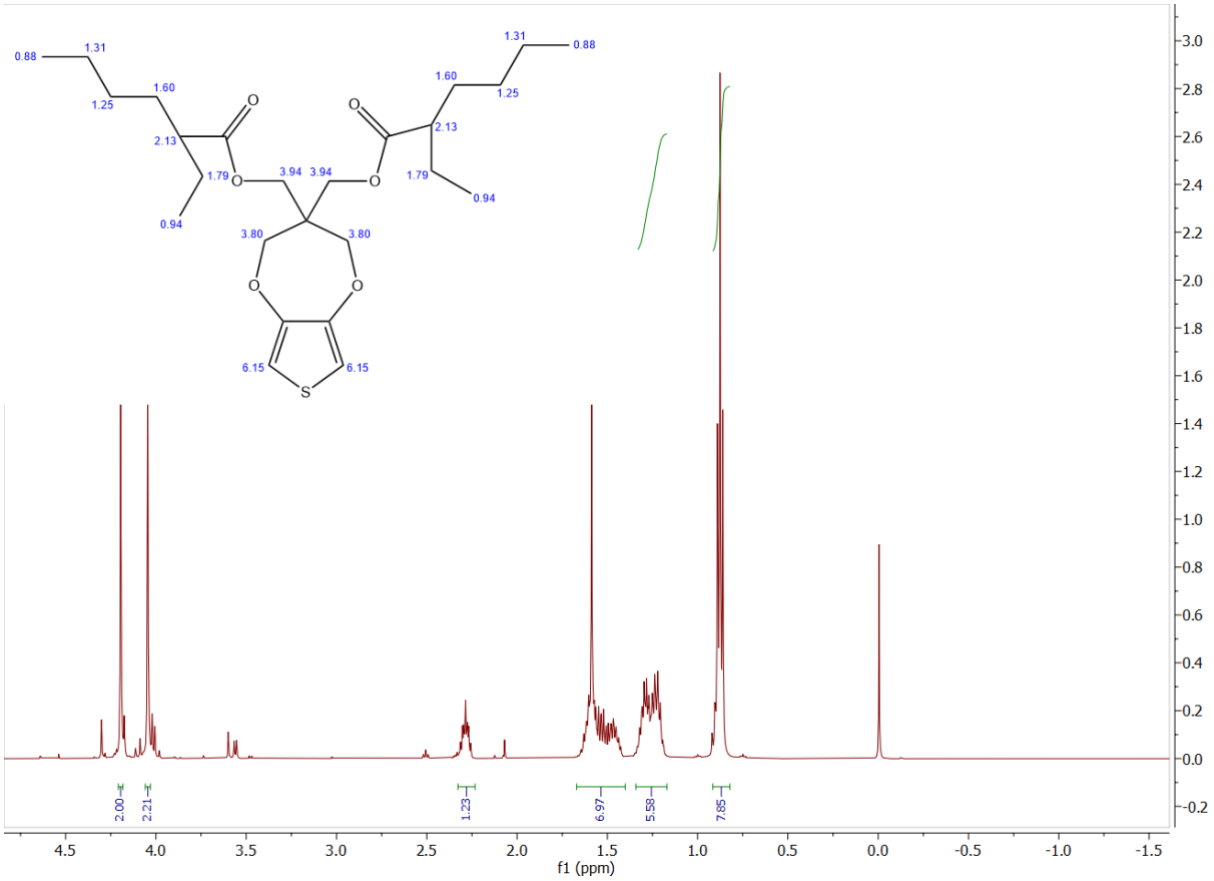

Figure S3. [1]H NMR spectra of ProDOT bis(2-ethylhexanoate) derivative

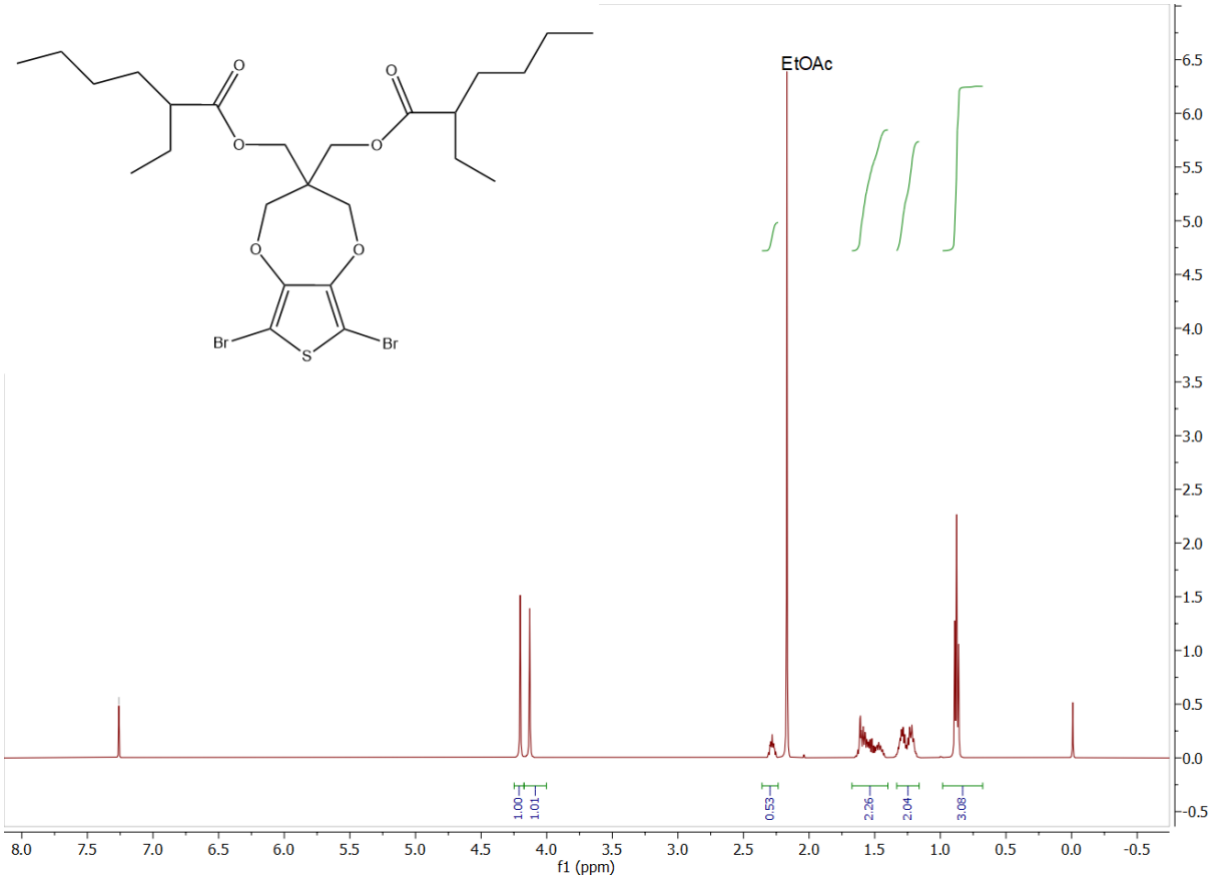

Figure S4. [1]H NMR spectra of ProDOT(EH)-Br_2

Here is the calculation of oxidized sulfur content:

General formula

$$A_{total} = \sum A_i \text{Relative area } (\%) = \frac{A_i}{A_{total}} \times 100$$

Neutral thiophene sulfur area

$$A_{neutral} = A(S\,2p_{3/2}) + A(S\,2p_{1/2})$$

Total S 2p area

$$A_{total} = A(S\,2p_{3/2}) + A(S\,2p_{1/2}) + A_{oxidized}$$

Relative neutral thiophene sulfur contribution

$$\text{Neutral thiophene sulfur } (\%) = \frac{A_{neutral}}{A_{total}} \times 100$$

Relative oxidized sulfur contribution

$$\text{Oxidized sulfur } (\%) = \frac{A_{oxidized}}{A_{total}} \times 100$$

Individual S 2p component contribution

$$S\,2p_{3/2} \text{ contribution } (\%) = \frac{A(S\,2p_{3/2})}{A_{total}} \times 100 S\,2p_{1/2} \text{ contribution } (\%) = \frac{A(S\,2p_{1/2})}{A_{total}} \times 100$$

Table S1. Fitted S 2p peak positions, assignments, peak areas, and calculated sulfur contributions for PProDOT-EHE and PProDOT-OH.

Sample	**Center (eV)**	**Assignment**	**Peak area, Ai**	**Total S 2p area, Atotal**	**Relative contribution (%)**
PProDOT-EHE	163.7	Neutral thiophene sulfur	20155	25543	78.9
PProDOT-EHE	167.8	Oxidized sulfur species	5388	25543	21.1
PProDOT-OH	163.4	S $2p_{3/2}$ neutral thiophene sulfur	5747	37511	15.3
PProDOT-OH	164.7	S $2p_{1/2}$ neutral thiophene sulfur	3618	37511	9.6
PProDOT-OH	168.4	Oxidized sulfur species	28146	37511	75.0

Note: Atotal = ΣAi. Relative contribution (%) = (Ai / Atotal) × 100. For PProDOT-OH, the combined neutral thiophene sulfur contribution is 15.3% + 9.6% = 24.9%, approximately 25.0%.

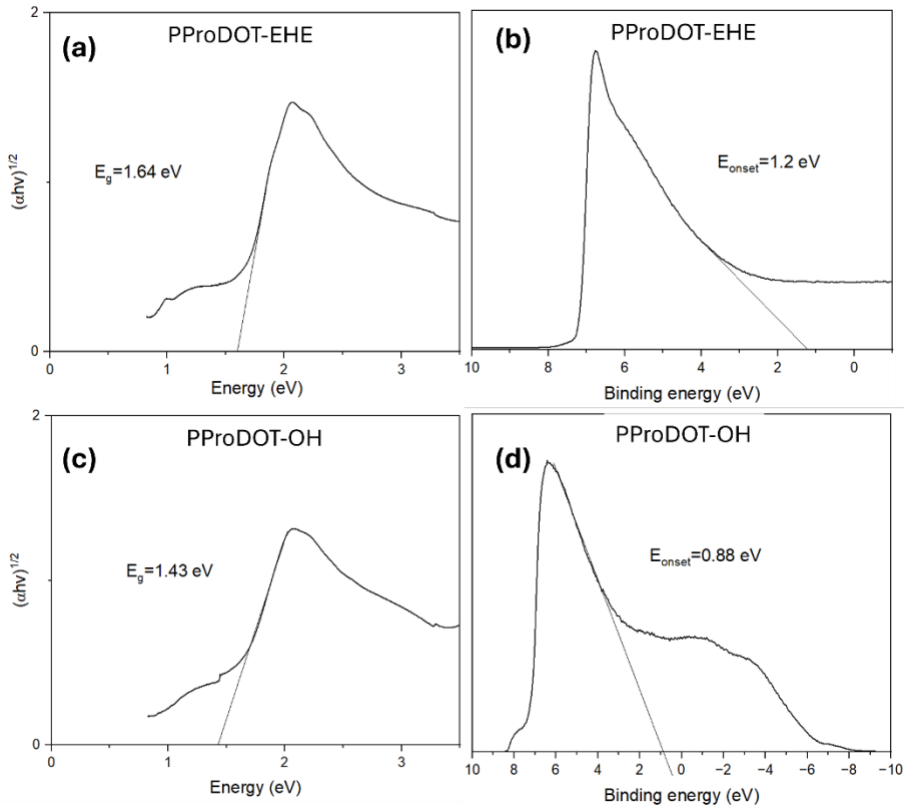

Figure S5. Determination of optical band gaps and UPS onset energies of PProDOT-EHE and PProDOT-OH: (a,c) Tauc plots obtained from UV–Vis absorption spectra and (b,d) UPS spectra used to estimate the electronic energy levels.

Table S2. Electronic energy-level parameters of PProDOT-EHE and PProDOT-OH estimated from UV–Vis Tauc plots and UPS analysis.

Sample	Ecutoff, KE (eV)	EF, KE (eV)	EF − Ecutoff (eV)	Φ/WF (eV)	Eonset (eV)	HOMO (eV)	Eg (eV)	LUMO (eV)
PProDOT(EHE)	14.02	30.54	16.52	4.70	1.20	−5.90	1.64	−4.26
PProDOT(OH)	13.98	30.89	16.91	4.31	0.88	−5.19	1.43	−3.76

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[1] J. F. Ponder et al., "Significant Enhancement of the Electrical Conductivity of Conjugated Polymers by Post-Processing Side Chain Removal," J. Am. Chem. Soc., vol. 144, no. 3, pp. 1351–1360, Jan. 2022, doi: 10.1021/jacs.1c11558.

[2] C. Beaumont et al., "Water-Processable Self-Doped Conducting Polymers via Direct (Hetero)arylation Polymerization," Macromolecules, vol. 54, no. 12, pp. 5464–5472, Jun. 2021, doi: 10.1021/acs.macromol.1c00847.

[3] J. F. Ponder et al., "Metal-like Charge Transport in PEDOT(OH) Films by Post-processing Side Chain Removal from a Soluble Precursor Polymer," Angew. Chem. Int. Ed., vol. 62, no. 1, Jan. 2023, doi: 10.1002/anie.202211600.