

Supporting Information

Transparent Electrochromic Polymers with High Optical Contrast and Contrast Ratio

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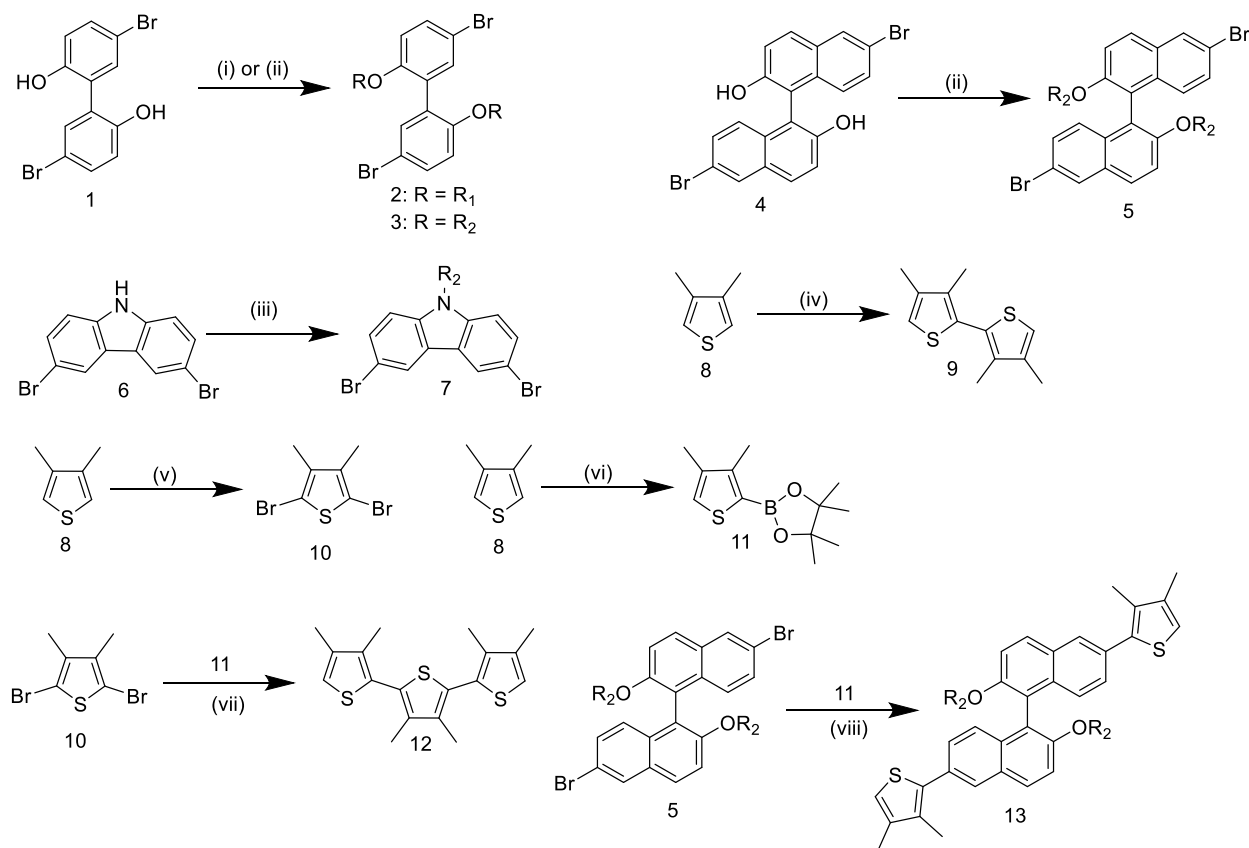
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1. Supplementary Synthesis Methods

All reagents were purchased from Sigma Aldrich, TCI, Oakwood Chemical or Combi-Blocks and used without further purification unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 or Mercury 300 at 293 K with deuterized chloroform as solvent. Size exclusive chromatography (SEC) was performed in tetrahydrofuran under room temperature with calibration curve based on polystyrene standards.



Scheme S1. Reagents and conditions: (i) 2-chloroethyl methyl ether, potassium carbonate, potassium iodide, DMF, 65 °C, overnight, nitrogen; (ii) 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate, potassium carbonate, potassium iodide, DMF, 100 °C, overnight, nitrogen; (iii) 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate, tetrabutylammonium chloride, potassium hydroxide, toluene, water, 100 °C, 24 h, nitrogen; (iv) [hydroxy(tosyloxy)iodo]benzene, bromotrimethylsilane, hexafluoro-2-propanol, room temperature, 3 h, nitrogen; (v) NBS, tetrahydrofuran, 0 °C-rt, 2.5 h; (vi) *n*-BuLi, THF, -10 °C – room temperature, 30 min, nitrogen then, 2-isopropoxy-4,4,5,5-

tetramethyl[1,3,2]dioxaborolane, -10 °C – room temperature, 30 min, nitrogen; (vii) Pd(PPh₃)₄, potassium carbonate, water, toluene, reflux, overnight, nitrogen then methanol slurry; (viii) Pd(PPh₃)₄, potassium carbonate, water, toluene, reflux, overnight, nitrogen.

5,5'-Dibromobiphenyl-2,2'-diol 1

2,2' Biphenol (15.00 g, 80.55 mmol) and p-toluenesulfonic acid (19.20 g, 104.72 mmol) were dissolved in acetonitrile (150 mL). Subsequently, N-bromosuccinimide (28.67 g, 161.11 mmol) was added and the mixture was agitated overnight. The suspension was filtered, and the material was then purified by recrystallization from ethanol to afford **1** as a white powder (24.40 g, 88%).

5,5'-dibromo-2,2'-bis(2-methoxyethoxy)-1,1'-biphenyl 2

1 (40.00 g, 116.28 mmol) was dissolved in *N,N*-dimethylformamide (200 mL) under N₂. Potassium carbonate (62.28 g, 465.11 mmol) was added to the solution and the reaction mixture was stirred for 15 min, after which 2-chloroethyl methyl ether (32.98 g, 348.84 mmol) and potassium iodide (64.28 g, 465.11 mmol) were added. The reaction mixture was stirred at 65 °C overnight before being allowed to cool to room temperature. Deionized water (200 mL) was added, and the reaction mixture was extracted with ethyl acetate (4 × 100 mL). The combined organic extracts were dried over sodium sulphate, filtered, and the solvent was removed. The crude product was purified using automated preparative column chromatography with *n*-hexane: dichloromethane (1:0 to 1:1) as eluent to give **2** as a white powder (40.00 g, 75%). ¹H NMR (400 MHz, CD₃Cl₃): δ ppm 7.42–7.36 (m, 4H), 6.38 (d, *J* = 9.0 Hz, 2H), 4.04 (t, *J* = 5.0 Hz, 4H), 3.60 (t, *J* = 5.0 Hz, 4H), 3.31 (s, 6H); ¹³C NMR (MHz, CDCl₃): δ ppm 155.5, 134.3, 131.5, 128.6, 114.3, 112.8, 71.0, 68.6, 59.3; HRMS *m/z* calcd. for C₁₈H₂₀Br₂O₄⁺ [M+H]⁺ 458.9807, obsd. 458.9794.

5,5'-dibromo-2,2'-bis[2-(2-methoxyethoxy)ethoxy]-1,1'-biphenyl 3

1 (7.00 g, 20.35 mmol) was dissolved in *N,N*-dimethylformamide (50 mL) under N₂. Potassium carbonate (11.16 g, 40.70 mmol) was added to the solution and the reaction mixture was stirred for 15 min, after which 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (8.44 g, 61.05 mmol) were added. The reaction mixture was stirred at 100 °C overnight before being allowed to cool to

room temperature. Deionized water (100 mL) was added, and the reaction mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic extracts were dried over sodium sulphate, filtered, and the solvent was removed. The crude product was purified using automated preparative column chromatography with *n*-hexane: dichloromethane (1:0 to 1:1) as eluent to give **3** as a white powder (9.49 g, 85%). ¹H NMR (400 MHz, CD₃Cl₃): δ ppm 7.38-7.36 (m, 4H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.06 (t, *J* = 5.0 Hz, 4H), 3.70 (t, *J* = 5.0 Hz, 4H), 3.53-3.51 (m, 4H), 3.46-3.44 (m, 4H), 3.33 (s, 6H); ¹³C NMR (MHz, CDCl₃): δ ppm 155.4, 134.2, 131.5, 128.6, 114.0, 112.7, 72.0, 70.9, 69.6, 68.8, 59.1; HRMS *m/z* calcd. for C₂₂H₂₈Br₂O₆⁺ [M+H]⁺ 547.0331, obsd. 547.0352.

6,6'-dibromo-(1,1'-binaphthanlene)-2,2'-diol 4

A solution of bromine (8.63 g, 54.03 mmol) in dichloromethane (20 mL) was added dropwise to a solution of (1,1'-binaphthanlene)-2,2'-diol (5.73 g, 20.01 mmol) in dichloromethane (100 mL) over 15 min at −78 °C. The reaction mixture was stirred for 2 hours at −78 °C and then warmed gradually to room temperature for an additional 2 hours. The excess bromine was quenched by saturated aqueous sodium sulphite solution (50 mL) and stirred for 2 hours under room temperature. After extraction with dichloromethane (20 mL × 3), the combined organic layer was washed with brine (40 mL), dried over sodium sulfate, and concentrated in vacuo. The crude product was purified using automated preparative column chromatography with *n*-hexane: ethyl acetate (1:0 to 3:1) as eluent to give **4** as an off-white solid (8.89 g, quantitative).

6,6'-dibromo-2,2'-bis[2-(2-methoxyethoxy)ethoxy]-1,1'-binaphthalene 5

4 (7.000 g, 15.761 mmol) was dissolved in *N,N*-dimethylformamide (50 mL) under N₂. Potassium carbonate (6.535 g, 47.28 mmol) was added to the solution and the reaction mixture was stirred for 15 min, after which 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (8.648 g, 31.52 mmol) were added. The reaction mixture was stirred at 100 °C overnight before being allowed to cool to room temperature. Deionized water (100 mL) was added, and the reaction mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic extracts were dried over sodium sulphate, filtered, and the solvent was removed. The crude product was purified using automated preparative column chromatography with *n*-hexane: dichloromethane (1:0 to 1:1) as eluent to give

5 as a white powder (8.479 g, 83%). ¹H NMR (400 MHz, CD₃Cl₃): δ ppm 8.00 (d, *J* = 2.0 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 9.0, 2H), 7.27 (dd, *J* = 2.0 and 9.0 Hz, 2H) 6.99 (d, *J* = 9.0 Hz, 2H), 4.10 (t, *J* = 5.0 Hz, 4H), 3.53-3.41 (m, 4H), 3.25 (s, 6H), 3.18-3.10 (m, 8H); ¹³C NMR (MHz, CDCl₃): δ ppm 154.6, 132.5, 130.4, 129.8, 129.7, 128.6, 127.2, 119.9, 117.6, 116.3, 71.8, 70.6, 69.7, 69.6, 59.0; HRMS *m/z* calcd. for C₃₀H₃₂Br₂O₆⁺ [M+H]⁺ 647.064, obsd. 647.0669

3,6-dibromo-9-[2-(2-methoxyethoxy)ethyl]-9H-carbazole 7

A mixture of **6** (1.000 g, 3.08 mmol), 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (1.010 g, 3.69 mmol), potassium hydroxide (1.730 g, 30.77 mmol), tetrabutylammonium chloride (0.428 g, 1.42 mmol) was dissolved in toluene (10 mL) and water (1 mL) under N₂. The reaction mixture was stirred at 100 °C overnight before being allowed to cool to room temperature. Deionized water (100 mL) was added, and the reaction mixture was extracted with dichloromethane (4 × 50 mL). The combined organic extracts were dried over sodium sulphate, filtered, and the solvent was removed. The crude product was purified using automated preparative column chromatography with *n*-hexane: ethyl acetate (1:0 to 7:3) as eluent to give **7** as a white crystalline powder (1.127 g, 87%). ¹H NMR (400 MHz, CD₃Cl₃): δ ppm 8.09 (d, *J* = 2.0 Hz, 2H), 7.53 (dd, *J* = 2.0 and 9.0 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 4.41 (t, *J* = 6.0 Hz, 2H), 3.81 (t, *J* = 6.0 Hz, 2H), 3.48-3.46 (m, 2H), 3.39-3.37 (m, 2H), 3.28 (s, 3H); ¹³C NMR (MHz, CDCl₃): δ ppm 139.5, 130.0, 123.5, 123.1, 112.8, 110.7, 72.0, 70.9, 69.3, 59.1, 43.5; HRMS *m/z* calcd. for C₁₅H₁₃Br₂NO₂⁺ [M+H]⁺ 425.9704, obsd. 425.9719.*z*

3,3',4,4'-tetramethyl-2,2'-bithiophene 9

9 was synthesized following the literature procedure.¹ [Hydroxy(tosyloxy)iodo]benzene (1.75 g, 4.46 mmol) and then bromotrimethylsilane (1.36 g, 8.91 mmol) were added to a stirred solution of 3,4-diethylthiophene **8** (1.00 g, 8.91 mmol) in hexafluoroisopropanol (6 mL) at room temperature. After stirring for 3 h, dichloromethane (10 mL) and saturated aq. sodium bicarbonate (10 mL) was successively added to the reaction mixture with stirring. The organic layer was then separated, and the solvents evaporated to dryness. The crude product was purified using automated preparative column chromatography with *n*-hexane as eluent to give **9** as colorless crystals (1.39 g, 70%).

2,5-dibromo-3,4-dimethylthiophene 10

3,4-dimethylthiophene **8** (0.45 mg, 4.01 mmol) was dissolved in tetrahydrofuran (10 mL) and the reaction mixture was cooled in an ice bath. Subsequently, *N*-bromosuccinimide (1.57 g, 8.82 mmol) was added and the stirring solution was warm to room temperature over 2.5 h. Deionized water (50 mL) was added, and the reaction mixture was extracted with ethyl acetate (4 × 20 mL). The combined organic extracts were dried over sodium sulphate, filtered, and the solvent was removed. The crude product was purified using column chromatography with *n*-hexane as eluent to give **10** as pale-yellow oil (1.08 g, quantitative).

2-(3,4-dimethylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11

11 was synthesized following the literature procedure.² *n*-Butyllithium (1.43 g, 22.28 mmol) was added dropwise to a solution of 3,4-dimethylthiophene **8** (2.50 g, 22.28 mmol) in anhydrous tetrahydrofuran (10 mL), stirred at -10 °C. The solution was stirred at -10 °C for 30 minutes and then allowed to warm to ambient temperature. The solution was stirred for an additional hour before cooling it again to -10 °C. A solution of 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxoborolane (4.56 g, 24.51 mmol) in anhydrous tetrahydrofuran (10 mL) was added to the reaction mixture and the stirring was continued for 30 minutes. The reaction was quenched with an aqueous sodium bicarbonate solution (100 mL) and the product was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were dried over anhydrous sodium sulphate, filtered and the solvent was removed to afford **11** as a white powder (5.31 g, quantitative).

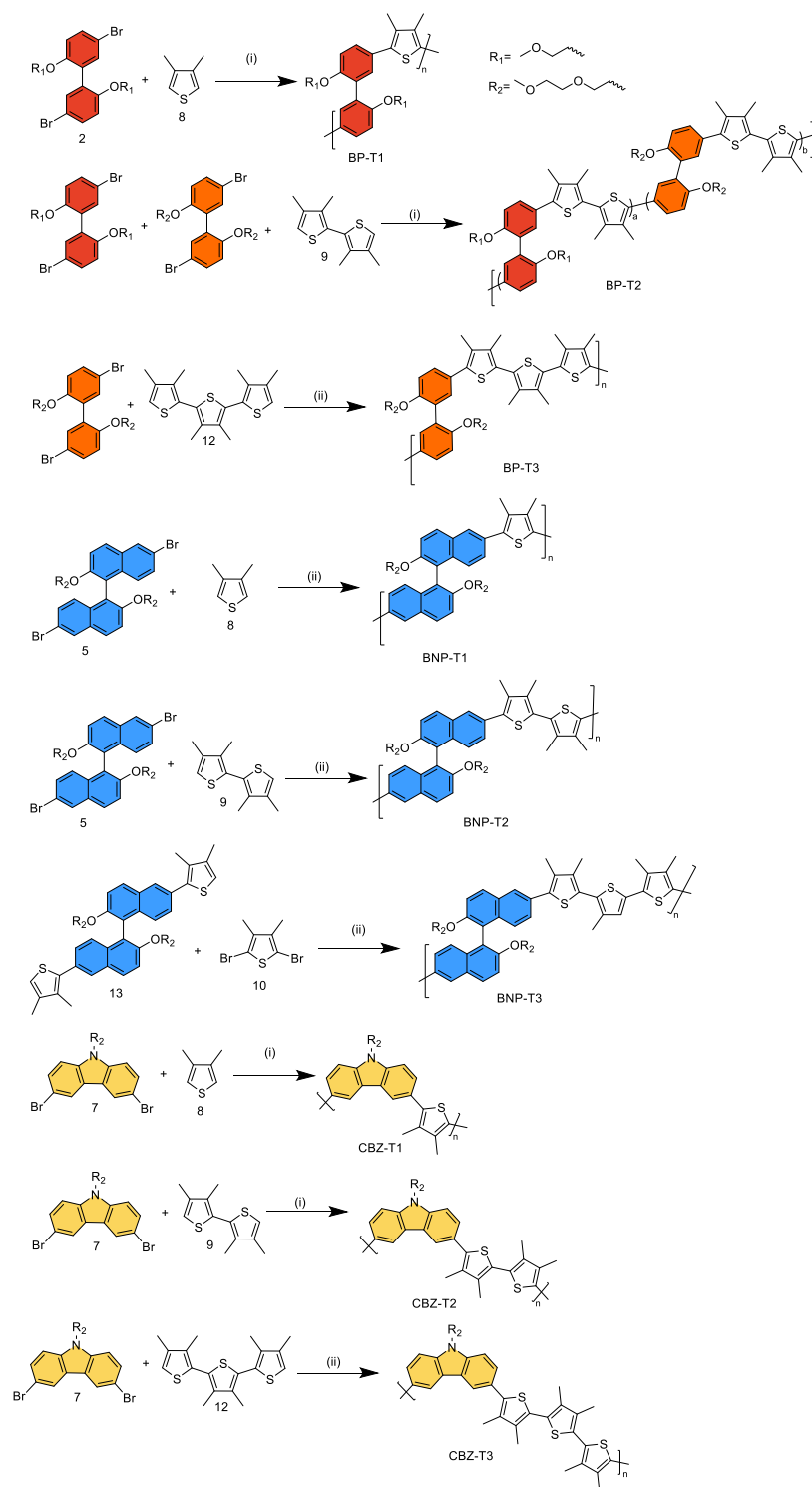
3,3',3'',4,4',4''-hexamethyl-2,2':5',2''-terthiophene 12

A mixture of **10** (0.35 g, 1.28 mmol), **11** (0.70 g, 2.94 mmol), potassium carbonate (3.53 g, 25.56 mmol), deionized water (5 mL), and toluene (8 mL) was subjected to three freeze–pump–thaw cycles, followed by placing under argon. Tetrakis(triphenylphosphine)palladium(0) (0.074 g, 5 mol%) was added to the reaction mixture followed by one further freeze–pump–thaw cycle, backfilling with argon. The reaction mixture was heated at reflux overnight before being allowed

to cool to room temperature. Deionized water (50 mL) was added, and the mixture was extracted with ethyl acetate (4 × 20 mL). The combined organic extracts were dried over anhydrous sodium sulphate, filtered, and the solvent was removed. The crude product was purified using column chromatography over silica with *n*-hexane as eluent to give **12** as a white powder (0.30 g, 71%). ¹H NMR (400 MHz, CD₃Cl₃): δ ppm 9.95 (s, 2H), 2.21 (s, 6H), 2.08 (d, *J* = 3.5 Hz, 12H); ¹³C NMR (MHz, CDCl₃): δ ppm 138.1, 136.5, 136.3, 130.2, 129.8, 120.8, 15.5, 14.2, 13.6; HRMS *m/z* calcd. for C₂₂H₂₈Br₂O₆⁺ [M+H]⁺ 333.0805, obsd. 333.0812.

2,2'-[2,2'-bis(2-{2-methoxyethoxy}ethoxy)-(1,1'-binaphthalene)-6,6'-diyl]bis(3,4-dimethylthiophene) 13

A mixture of **5** (2.000 g, 3.08 mmol), **11** (1.840 g, 7.71 mmol), potassium carbonate (4.26 g, 30.85 mmol), tetrabutylammonium chloride (0.857 g, 3.08 mmol) deionized water (5 mL), and toluene (10 mL) was subjected to three freeze–pump–thaw cycles, followed by placing under argon. Tetrakis(triphenylphosphine)palladium(0) (0.178 g, 5 mol%) was added to the reaction mixture followed by one further freeze–pump–thaw cycle, backfilling with argon. The reaction mixture was heated at reflux overnight before being allowed to cool to room temperature. Deionized water (100 mL) was added, and the mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic extracts were dried over anhydrous sodium sulphate, filtered, and the solvent was removed. The crude product was purified using MPLC over silica with *n*-hexane as eluent to give **13** as yellow sticky solid (1.752 g, 80%). ¹H NMR (400 MHz, CD₃Cl₃): δ ppm 7.96 (d, *J* = 9.0 Hz, 2H), 7.90 d, *J* = 2.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.37-7.34 (m, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 1.0 Hz, 2H), 4.15 (t, *J* = 5.0 Hz, 4H), 3.58-3.47 (m, 4H), 3.23 (s, 6H), 3.19-3.11 (m, 8H), 2.24-2.22 (m, 12H); ¹³C NMR (MHz, CDCl₃): δ ppm 154.7, 138.8, 138.3, 133.12, 133.1, 130.8, 129.6, 129.4, 128.1, 127.9, 125.8, 120.4, 119.3, 116.1; HRMS *m/z* calcd. for C₄₂H₄₆O₆S₂⁺ [M+H]⁺ 711.2814, obsd. 711.2842.



Scheme S2. Reagents and conditions: (i) potassium carbonate, palladium chloride, pivalic acid, DMAc, 120 °C, 36 h, nitrogen; (ii) potassium carbonate, palladium acetate, pivalic acid, DMAc, 120 °C, 36 h, nitrogen.

BP-T1

2 (0.500 g, 1.09 mmol), **8** (0.122 g, 1.09 mmol), potassium carbonate (0.451 g, 3.26 mmol), palladium chloride (0.08 g, 0.04 mmol), and pivalic acid (0.033 g, 0.33 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (2 mL) was added to the solvent and the reaction mixture was purged with nitrogen for 30 min. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in *vacuo*. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The beige powder was then purified via Soxhlet extraction with hexane, acetone and chloroform. The mixture was then concentrated under *vacuo* and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **BP-T1** as a beige powder (0.400 g, 87%). $T_d(5\%) = 386\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 7.46 (d, $J = 2.5\text{ Hz}$, 2H), 7.38 (dd, $J = 2.5$ and 8.5 Hz , 2H), 7.04 (d, $J = 8.5\text{ Hz}$, 2H), 4.12 (dd, $J = 4.5$ and 5.0 Hz , 4H), 3.63 (dd, $J = 4.5$ and 5.0 Hz , 4H), 3.24 (s, 6H), 2.23 (s, 6H); GPC: $\overline{M}_w = 65992\text{ Da}$; $\overline{M}_n = 11626\text{ Da}$; $\overline{D} = 5.6$.

BP-T2

2 (0.103 g, 0.22 mmol), **3** (0.123 g, 0.22 mmol), **9** (0.100 g, 0.45 mmol), potassium carbonate (0.186 g, 1.35 mmol), palladium chloride (0.003 g, 0.02 mmol), and pivalic acid (0.014 g, 0.13 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (1 mL) was added to the solvent and the reaction mixture was subjected to three freeze-pump-thaw cycles backfilling with nitrogen. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in *vacuo*. The crude was

dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The beige powder was then purified via Soxhlet extraction with hexane, acetone and chloroform. The mixture was then concentrated under vacuo and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **BP-T2** as a beige powder (0.428 g, 84%). $T_d(5\%) = 388\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 7.45 (dd, $J = 2.5$ and 8.5 Hz, 4H), 7.39 (dd, $J = 2.5$ and 8.5 Hz, 4H), 7.03-6.99 (m, 4H), 4.15-4.11 (m, 8H), 3.74 (t, $J = 5.0$ Hz, 4H), 3.63 (t, $J = 5.0$ Hz, 4H), 3.49-3.47 (m, 4H), 3.35-3.33 (m, 4H), 3.29-3.25 (m, 12 H), 2.24 (s, 12H), 2.12 (s, 12H); GPC: $\overline{M}_w = 66950$ Da; $\overline{M}_n = 13969$ Da; $\overline{D} = 4.8$.

BP-T3

3 (0.120 g, 0.36 mmol), **12** (0.199 g, 0.36 mmol), potassium carbonate (0.130 g, 0.94 mmol), palladium acetate (0.002 g, 0.007 mmol), and pivalic acid (0.111 g, 0.12 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (1 mL) was added to the solvent and the reaction mixture was three freeze-pump-thaw cycles backfilling with nitrogen. The reaction mixture was heated at $120\text{ }^\circ\text{C}$ for 24 h. Stopped the reaction and added chloroform (10 mL). Washed the reaction mixture with deionized water (10 mL) and extracted the aqueous phase with chloroform (3 X 20 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in vacuo. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The beige powder was then purified via Soxhlet extraction with hexane and chloroform. The mixture was then concentrated under vacuo and then the solution was poured into vigorously stirred methanol (250 mL). The precipitate was collected at the filter and dried under a vacuum to afford **BP-T3** as a beige powder (0.674 g, 90%). $T_d(5\%) = 399\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 7.45(4)-7.44(8) (m, 2H), 7.39 (dd, $J = 2.5$ and 8.5 Hz, 2H), 7.01 (d, $J = 8.5$ Hz, 2H), 4.15 (d, $J = 5.0$ Hz, 4H), 3.75 (d, $J = 5.0$ Hz, 4H), 3.50-3.47 (m, 4H), 3.36-3.24 (m, 4H), 3.39 (s, 6H), 2.24 (s, 6H), 2.13 (s, 12H); GPC: $\overline{M}_w = 64950$ Da; $\overline{M}_n = 29059$ Da; $\overline{D} = 2.2$.

BNP-T1

5 (0.300 g, 0.46 mmol), **8** (0.519 g, 0.46 mmol), potassium carbonate (0.166 g, 1.20 mmol), palladium acetate (0.002 g, 0.009 mmol), and pivalic acid (0.142 g, 0.138 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (1.2 mL) was added to the solvent and the reaction mixture was purged with nitrogen for 30 min. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (10 mL). Washed the reaction mixture with deionized water (10 mL) and extracted the aqueous phase with chloroform (3 X 20 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in vacuo. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The beige powder was then purified via Soxhlet extraction with hexane and chloroform. The mixture was then concentrated under vacuo and then the solution was poured into vigorously stirred methanol (250 mL). The precipitate was collected at the filter and dried under a vacuum to afford **BNP-T1** as a beige powder (0.547 g, 87%). $T_d(5\%) = 397\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 7.97-7.95 (m, 4H), 7.46-7.39 (m, 4H), 7.24 (s, 2H), 4.15 (t, $J = 5.0\text{ Hz}$, 4H), 3.54-3.51 (m, 4H), 3.22-3.14 (m, 14H), 2.29 (s, 6H); GPC: $\overline{M}_w = 27972\text{ Da}$; $\overline{M}_n = 8224\text{ Da}$; $D = 3.4$.

BNP-T2

5 (0.200 g, 0.31 mmol), **9** (0.686 g, 0.31 mmol), potassium carbonate (0.111 g, 0.80 mmol), palladium acetate (0.001 g, 0.006 mmol), and pivalic acid (0.010 g, 0.09 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (1 mL) was added to the solvent and the reaction mixture was subjected to three freeze-pump-thaw cycles backfilling with nitrogen. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in vacuo. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The beige powder was then purified via Soxhlet extraction with hexane, acetone and chloroform. The mixture was then

concentrated under vacuo and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **BNP-T2** as a beige powder (0.428 g, 84%). $T_d(5\%) = 390\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 7.97-7.94 (m, 4H), 7.46-7.38 (m, 4H), 7.24 (s, 2H), 4.15 (t, $J = 5.0$ Hz, 4H), 3.56-3.48 (m, 4H), 3.23 (s, 6H), 3.19-3.11 (m, 8H), 2.28 (s, 6H), 2.16 (s, 6H); GPC: $\overline{M}_w = 14743$ Da; $\overline{M}_n = 7879$ Da; $D = 1.9$.

BNP-T3

13 (0.300 g, 0.42 mmol), **11** (0.114 g, 0.42 mmol), potassium carbonate (0.151 g, 1.10 mmol), palladium acetate (0.002 g, 0.008 mmol), and pivalic acid (0.013 g, 0.13 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (1 mL) was added to the solvent and the reaction mixture was subjected to three freeze-pump-thaw cycles backfilling with nitrogen. The reaction mixture was heated at $120\text{ }^\circ\text{C}$ for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in vacuo. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The yellow powder was then purified via Soxhlet extraction with hexane, acetone and chloroform. The mixture was then concentrated under vacuo and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **BNP-T3** as a yellow powder (0.340 g, 95%). $T_d(5\%) = 398\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 7.97-7.94 (m, 4H), 7.46-7.38 (m, 4H), 7.24 (s, 2H), 4.15 (t, $J = 5.0$ Hz 4H), 3.56-3.48 (m, 4H), 3.23 (s, 6H), 3.17-3.11 (m, 8H), 2.28 (s, 6H), 2.15 (s, 12H); GPC: $\overline{M}_w = 38519$ Da; $\overline{M}_n = 18719$ Da; $D = 2.1$.

CBZ-T1

7 (0.500 g, 1.17 mmol), **8** (0.131 g, 1.17 mmol), potassium carbonate (0.49 g, 3.51 mmol), palladium chloride (0.08 g, 0.05 mmol), and pivalic acid (0.036 g, 0.35 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (2 mL) was added to the solvent and the

reaction mixture was purged with nitrogen for 30 min. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in *vacuo*. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The yellow powder was then purified via Soxhlet extraction with hexane, acetone, and chloroform. The mixture was then concentrated under *vacuo* and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **CBZ-T1** as a yellow powder (0.39 g, 88%). $T_d(5\%) = 399\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 8.22 (s, 2H), 7.63-7.49 (m, 4H), 4.52 (s, 2H), 3.90 (s, 2H), 3.53-3.43 (m, 4H), 3.30 (s, 3H), 6.03 (s, 6H); GPC: $\overline{M}_w = 29456\text{ Da}$; $\overline{M}_n = 7221\text{ Da}$; $D = 4.1$.

CBZ-T2

7 (0.436 g, 1.02 mmol), **9** (0.227 g, 1.02 mmol), potassium carbonate (0.423 g, 3.06 mmol), palladium chloride (0.007 g, 0.04 mmol), and pivalic acid (0.31 g, 0.31 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (2 mL) was added to the solvent and the reaction mixture was subjected to three freeze-pump-thaw cycles backfilling with nitrogen. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in *vacuo*. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The yellow powder was then purified via Soxhlet extraction with hexane, acetone and chloroform. The mixture was then concentrated under *vacuo* and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **CBZ-T2** as a yellow powder (0.45 g, 90%). $T_d(5\%) = 422\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 8.20 (s, 2H), 7.60-7.50 (m, 4H), 4.54 (s, 2H), 3.91 (m, 2H), 3.55-3.44 (m, 4H), 3.32 (s, 3H), 2.33-2.17 (m, 12H); GPC: $\overline{M}_w = 59268\text{ Da}$; $\overline{M}_n = 12941\text{ Da}$; $D = 4.6$.

CBZ-T3

5 (0.200 g, 0.47 mmol), **12** (0.156 g, 0.47 mmol), potassium carbonate (0.168 g, 1.20 mmol), palladium acetate (0.002 g, 0.009 mmol), and pivalic acid (0.014 g, 0.14 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under the high vacuum followed by the backfilling with nitrogen thrice. *N, N*-dimethylacetamide (5 mL) was added to the solvent and the reaction mixture was subjected to three freeze-pump-thaw cycles backfilling with nitrogen. The reaction mixture was heated at 120 °C for 36 h. Stopped the reaction and added chloroform (50 mL). Washed the reaction mixture with deionized water (50 mL) and extracted the aqueous phase with chloroform (3 X 50 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was dried in vacuo. The crude was dissolved in chloroform (3 mL) and the solution was poured into vigorously stirred methanol (150 mL). The yellow powder was then purified via Soxhlet extraction with hexane, acetone and chloroform. The mixture was then concentrated under vacuo and then the solution was poured into vigorously stirred methanol (150 mL). The precipitate was collected at the filter and dried under vacuum to afford **CBZ-T3** as a yellow powder (0.276 g, 94%). $T_d(5\%) = 426\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, CD_3Cl_3): δ ppm 8.18 (s, 2H), 7.60-7.49 (m, 4H), 4.54 (s, 2H), 3.91 (m, 2H), 3.55-3.44 (m, 4H), 3.31 (s, 3H), 2.30 (s, 6H), 2.19-2.18 (m, 12H); GPC: $\overline{M}_w = 32011\text{ Da}$; $\overline{M}_n = 14906\text{ Da}$; $D = 2.4$.

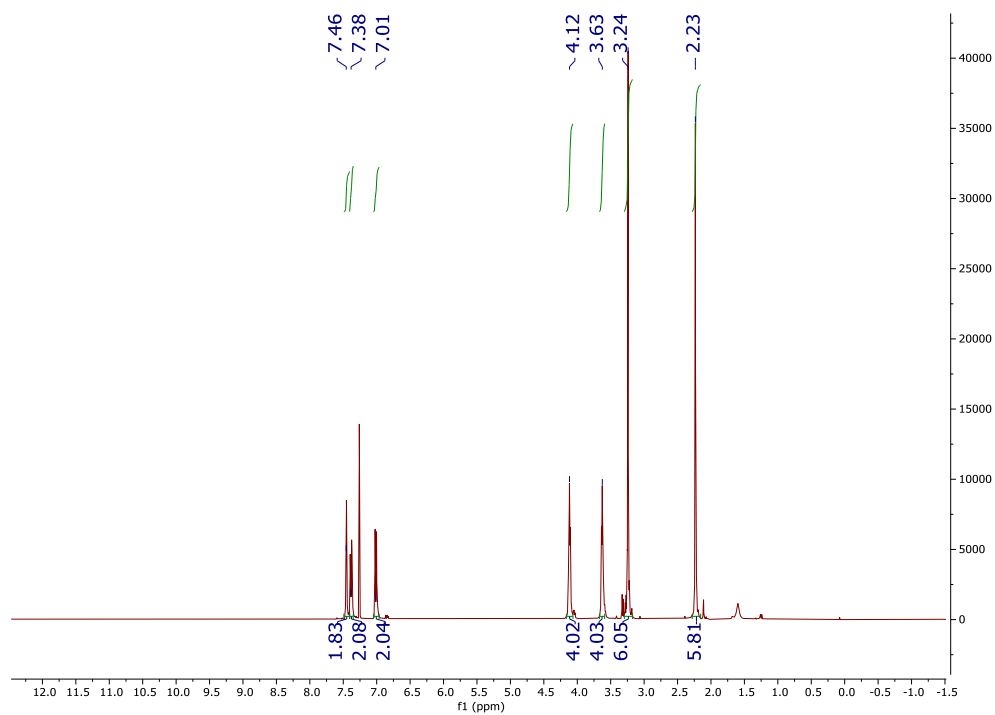


Figure S1. ^1H NMR spectrum of BP-T1 measured in deuterated chloroform.

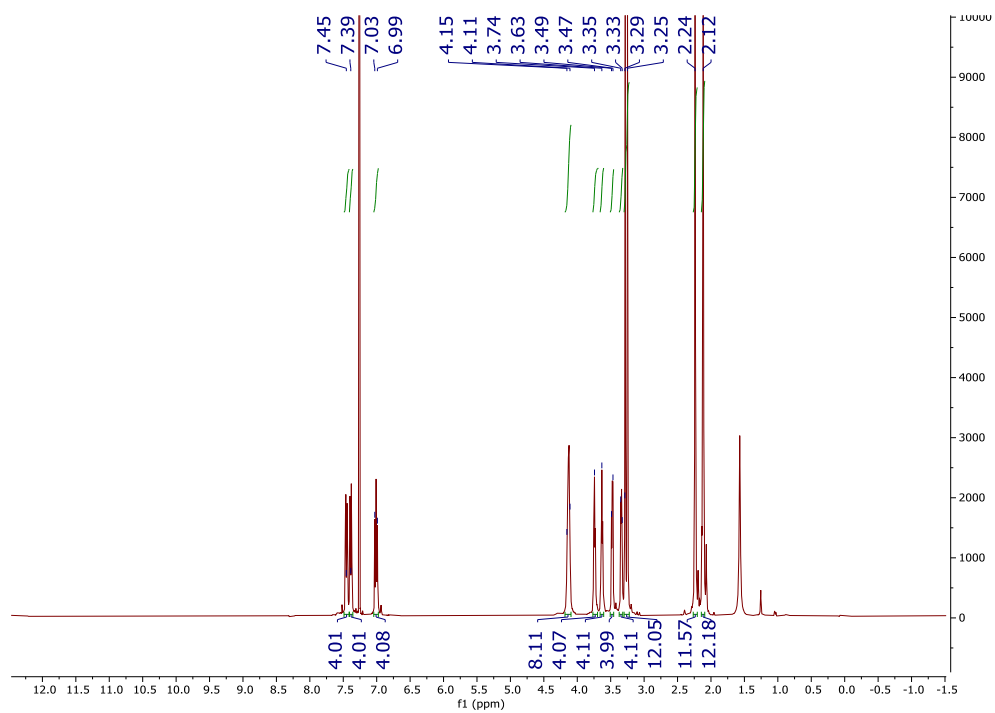


Figure S2. ^1H NMR spectrum of BP-T2 measured in deuterated chloroform.

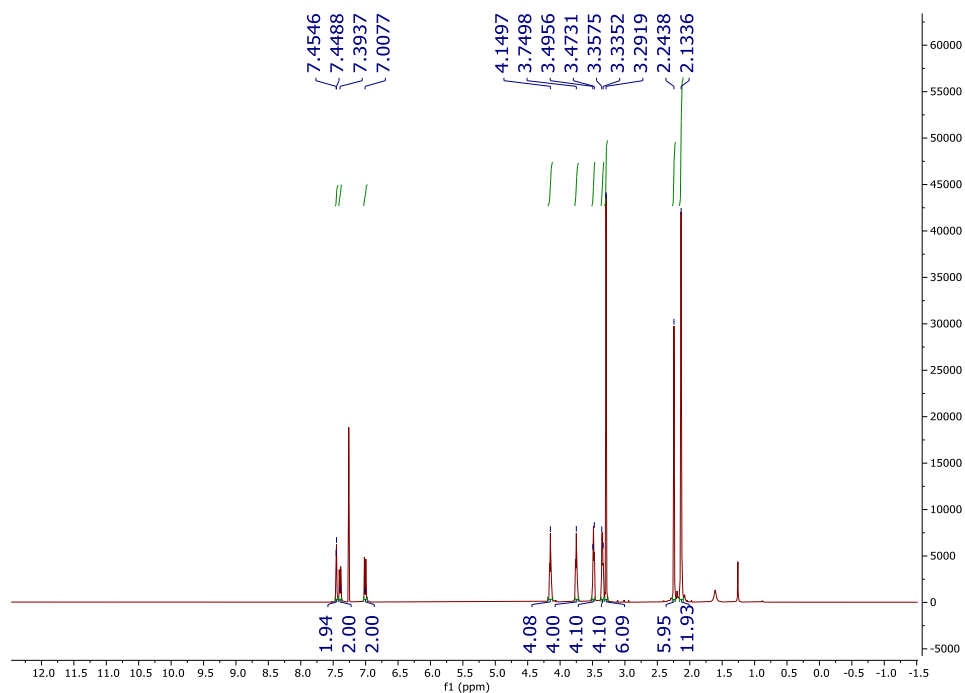


Figure S3. ^1H NMR spectrum of BP-T3 measured in deuterated chloroform.

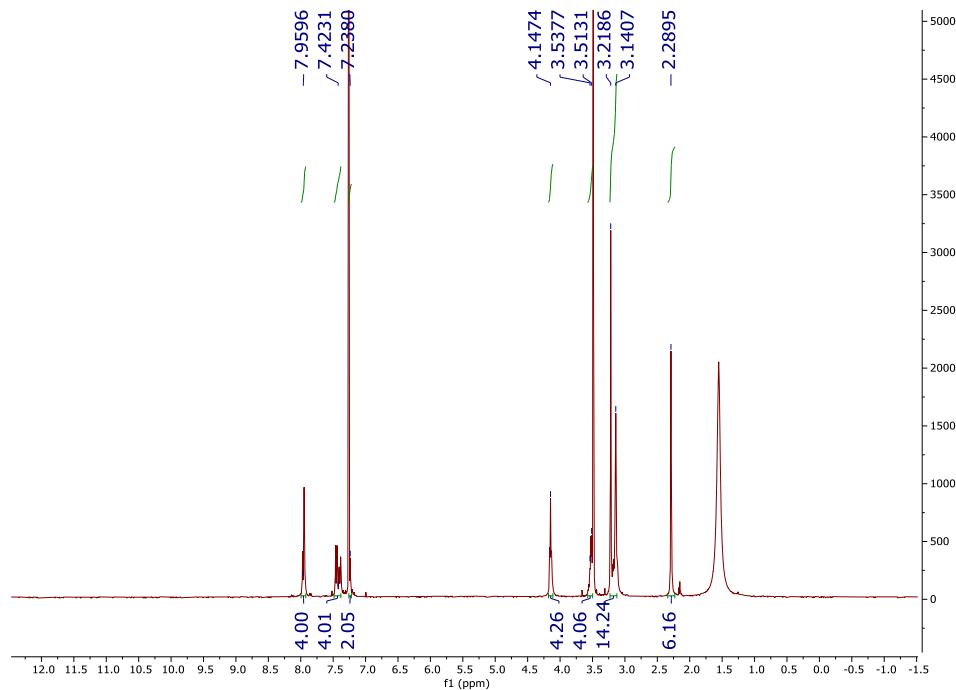


Figure S4. ^1H NMR spectrum of BNP-T1 measured in deuterated chloroform.

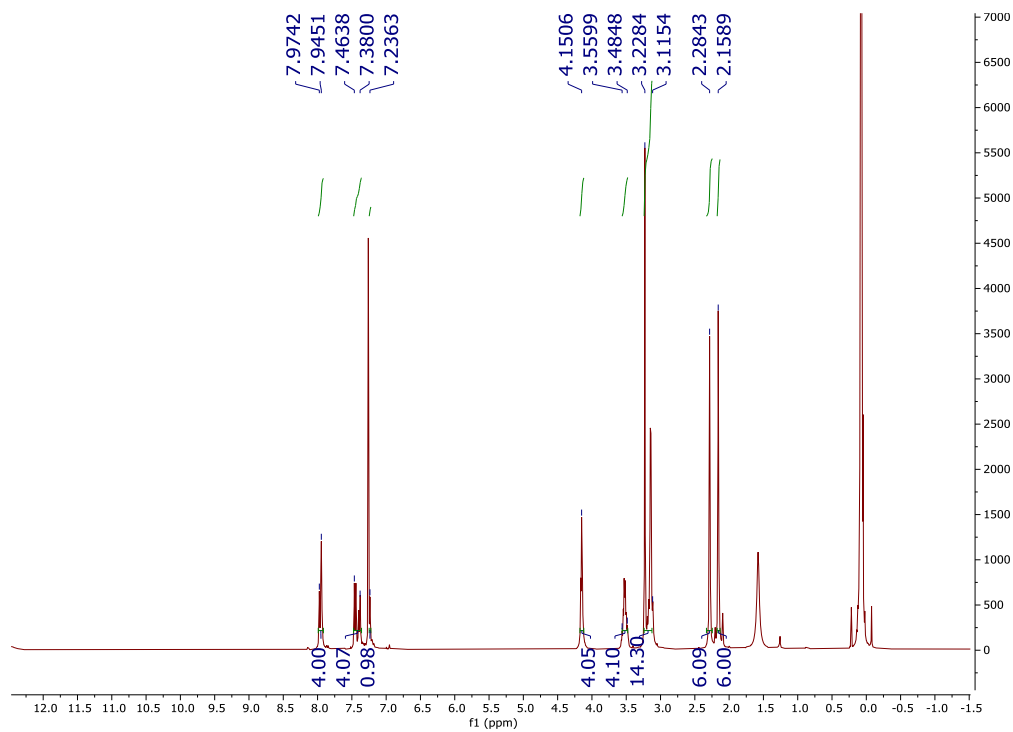


Figure S5. ¹H NMR spectrum of BNP-T2 measured in deuterated chloroform.

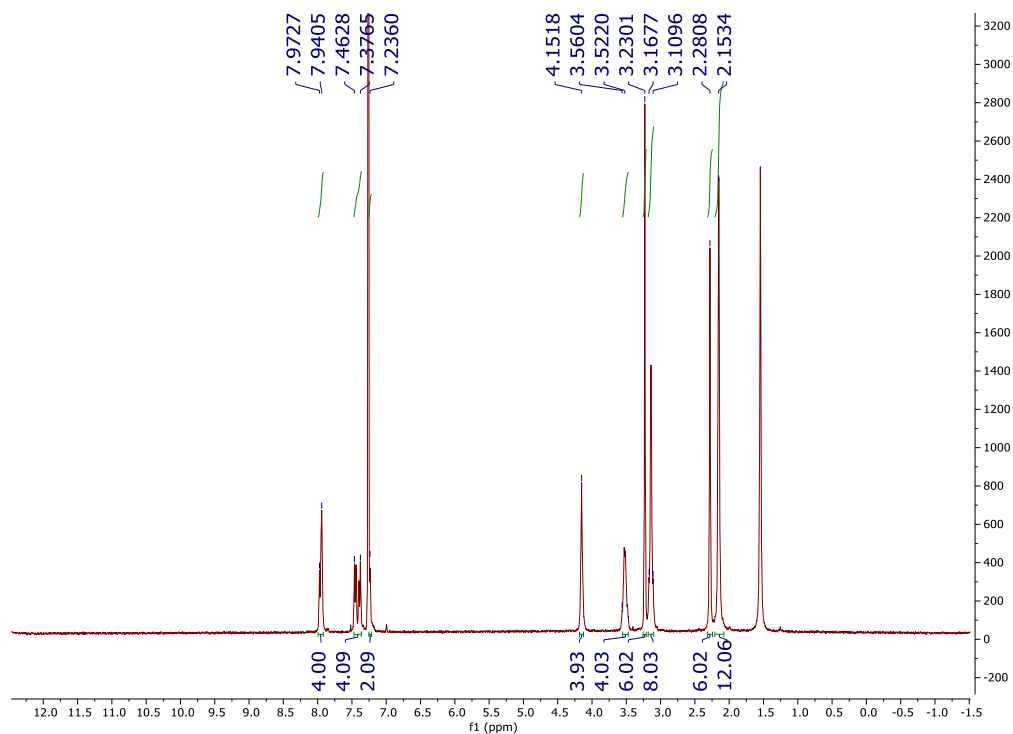


Figure S6. ¹H NMR spectrum of BNP-T3 measured in deuterated chloroform.

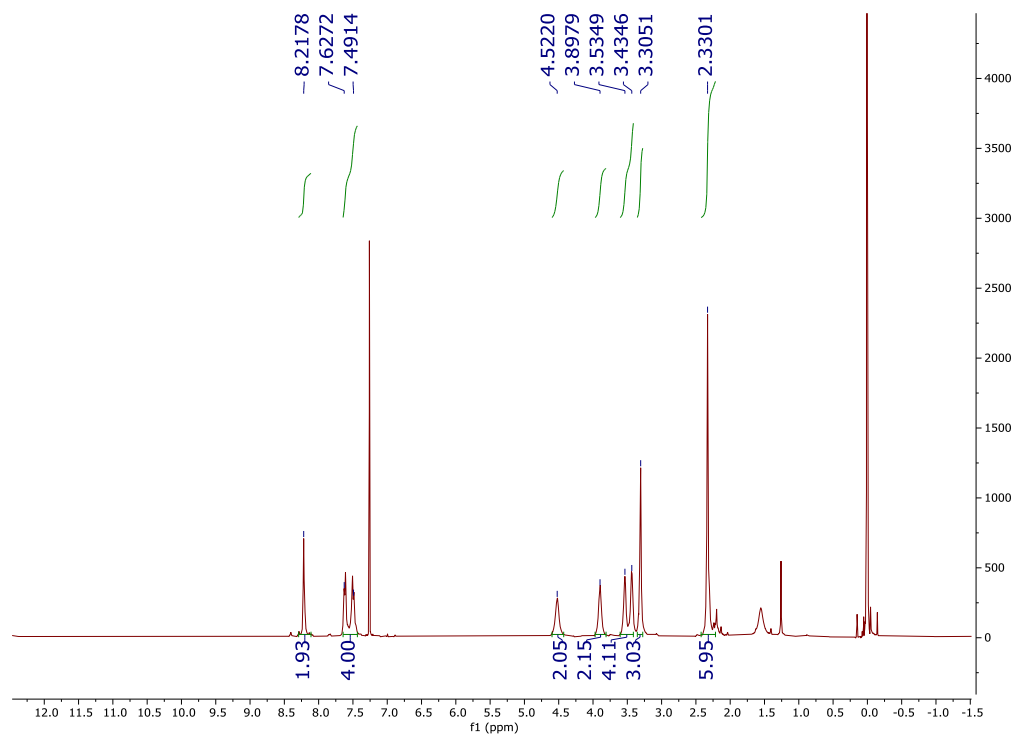


Figure S7. ¹H NMR spectrum of CBZ-T1 measured in deuterated chloroform.

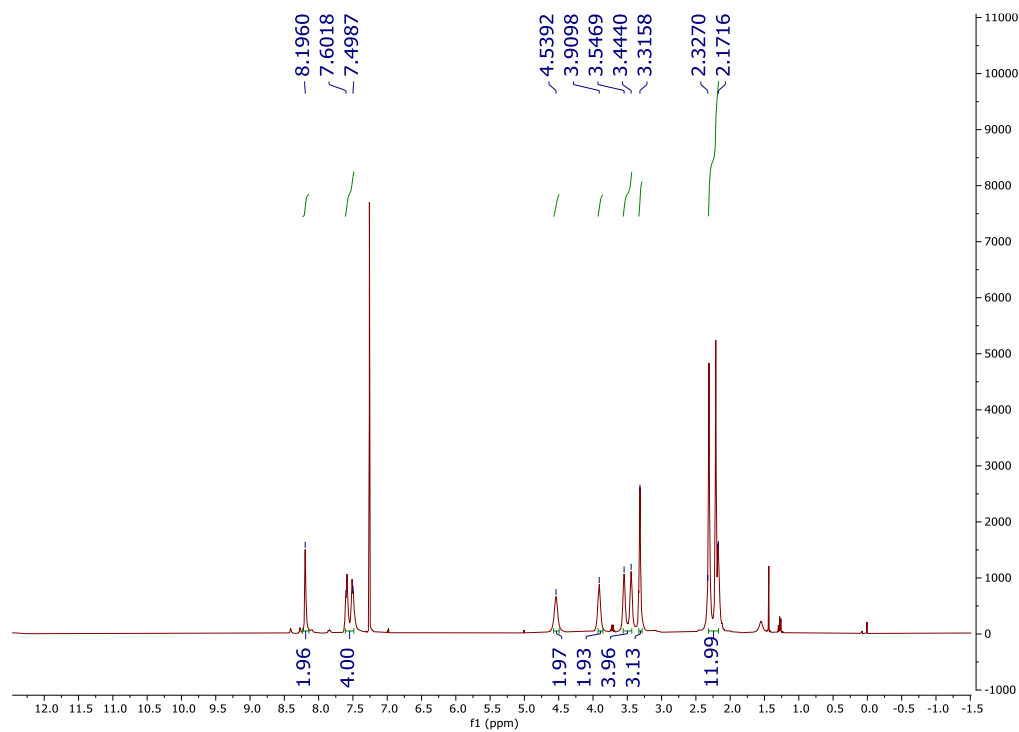


Figure S8. ¹H NMR spectrum of CBZ-T2 measured in deuterated chloroform.

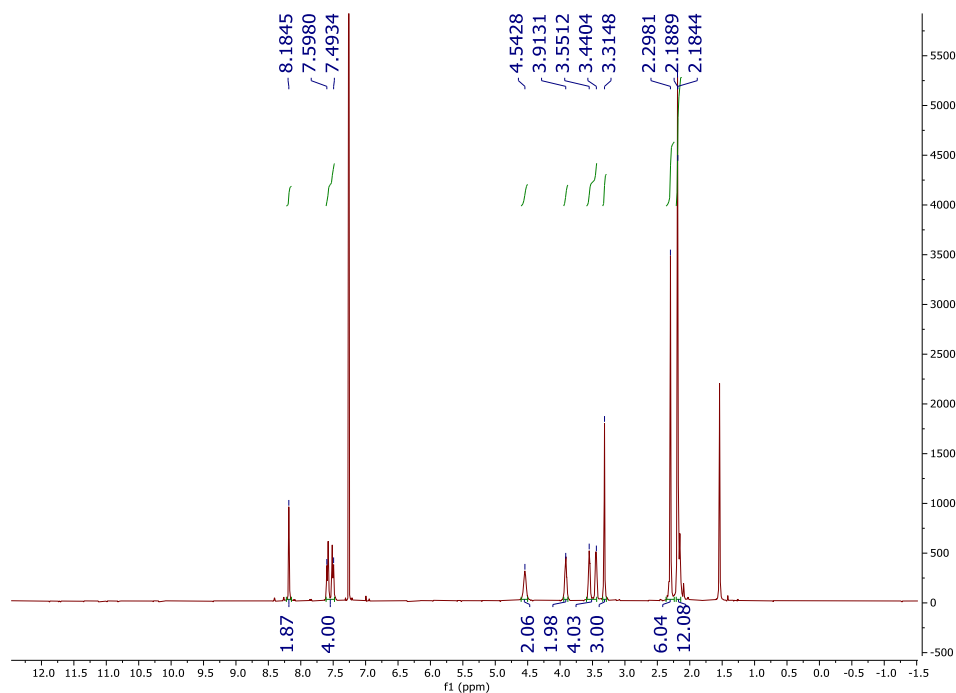


Figure S9. ^1H NMR spectrum of CBZ-T3 measured in deuterated chloroform.

2. Supplementary Figures

2.1 Polymer Characterization

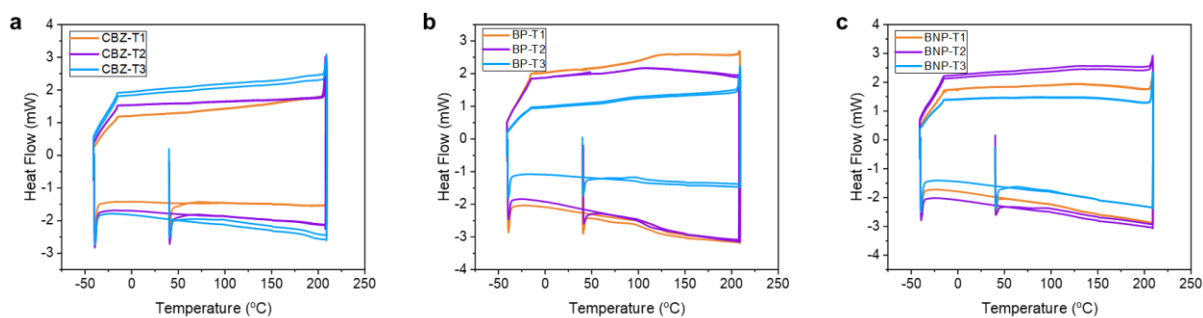


Figure. S10. DSC of (a) CBZ polymers, (b) BP polymers, and (c) BNP polymers between $-40\text{ }^{\circ}\text{C}$ and $210\text{ }^{\circ}\text{C}$ when heating and cooling at $10\text{ }^{\circ}\text{C}/\text{min}$.

The DCS experiments were performed at scan rates of $10\text{ }^{\circ}\text{C}/\text{min}$. All 9 polymers demonstrated the absence of any thermal phase transitions within the calibrated range of $-40\text{ }^{\circ}\text{C}$ and $210\text{ }^{\circ}\text{C}$.

2.2 DFT Calculations

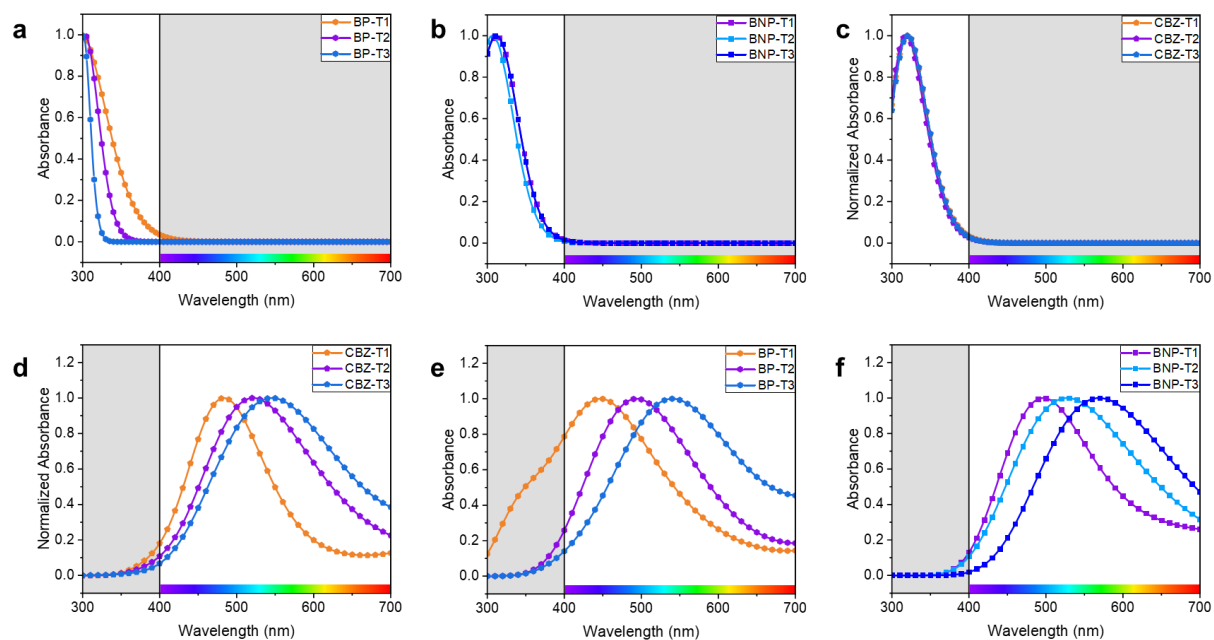


Figure S11. Calculated UV-Vis spectra for (a) BP (b) BNP, and (c) CBZ polymers in neutral state, and (a) BP (b) BNP, and (c) CBZ polymers in oxidized state.

2.3 Polymer solution electrochemical and optical characterization

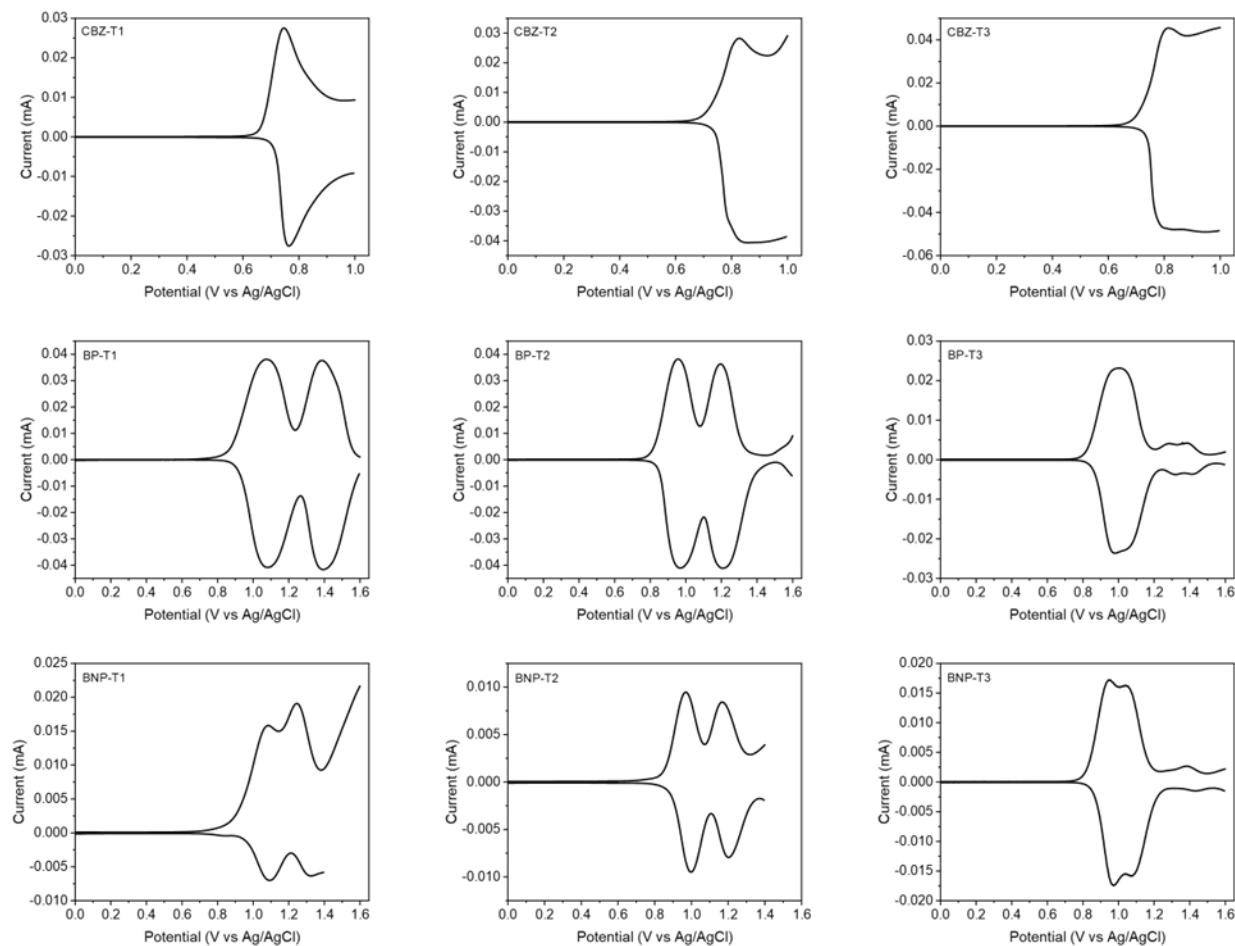


Figure S12. Solution phase DPV for polymers dissolved in DCM in concentration of 5mg/mL.

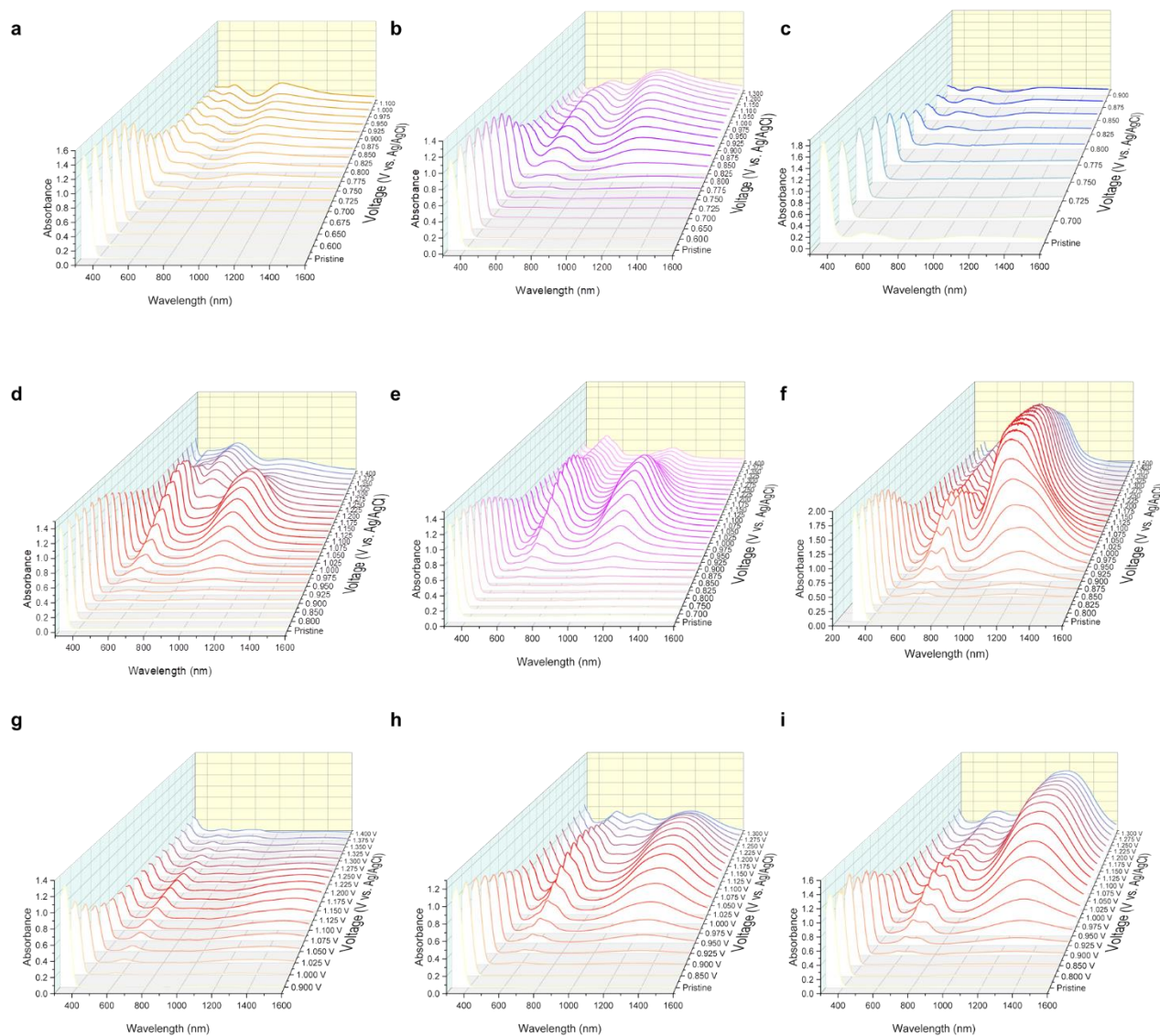


Figure S13. Spectro-electrochemistry of the polymer solution of (a) CBZ-T1 (b) CBZ-T2 (c) CBZ-T3 (d) BP-T1 (e) BP-T2 (f) BP-T3 (g) BNP-T1 (h) BNP-T2, and (i) BNP-T3 in 0.2 M TBAPF₆/DCM, conducted in an optically transparent thin-layer quartz cuvette equipped with a platinum honeycomb electrode vs Ag/AgCl.

2.4 Thin film characterization

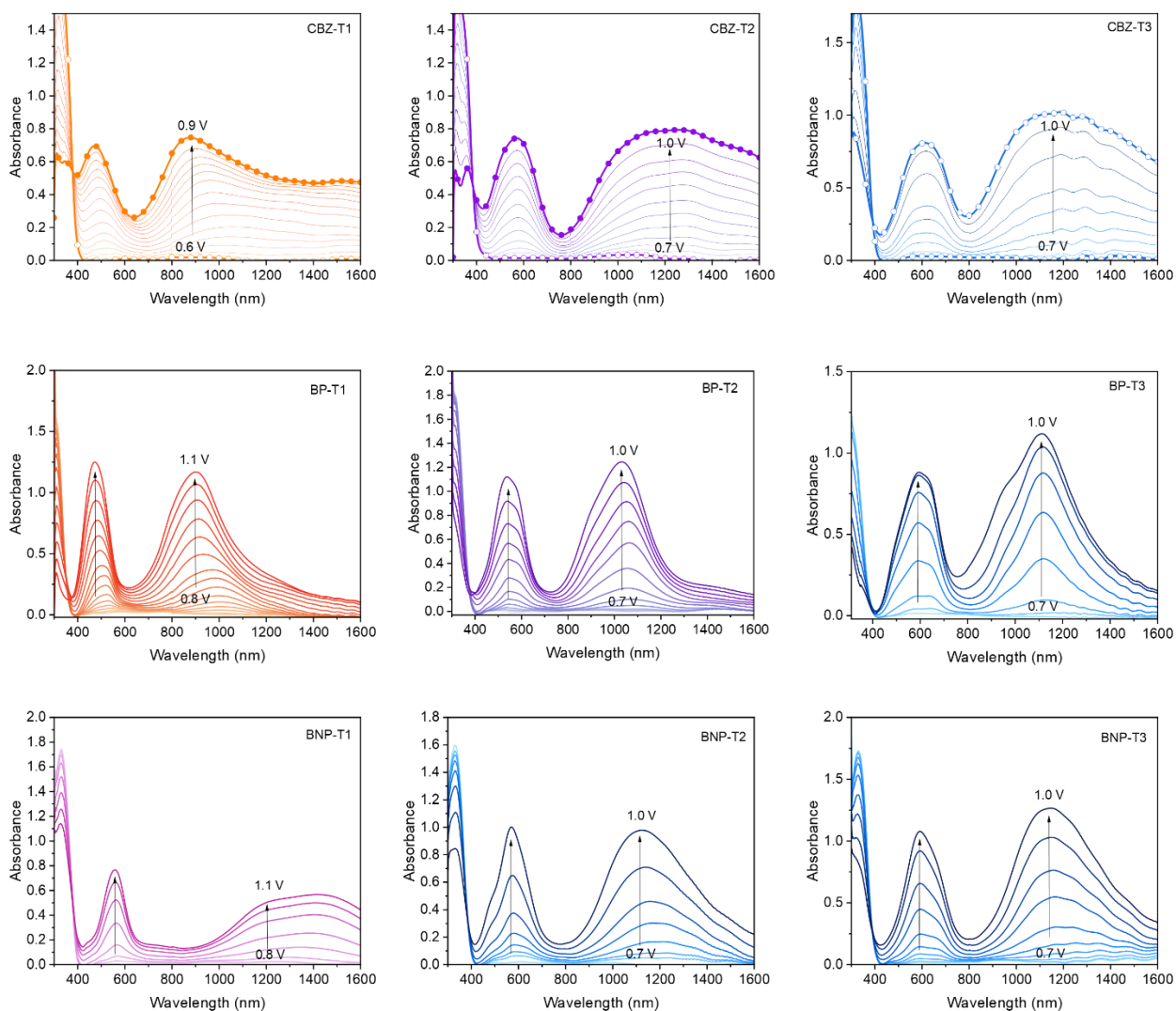


Figure S14. Spectro-electrochemical measurements of polymer films with potential increment of 0.025 V.

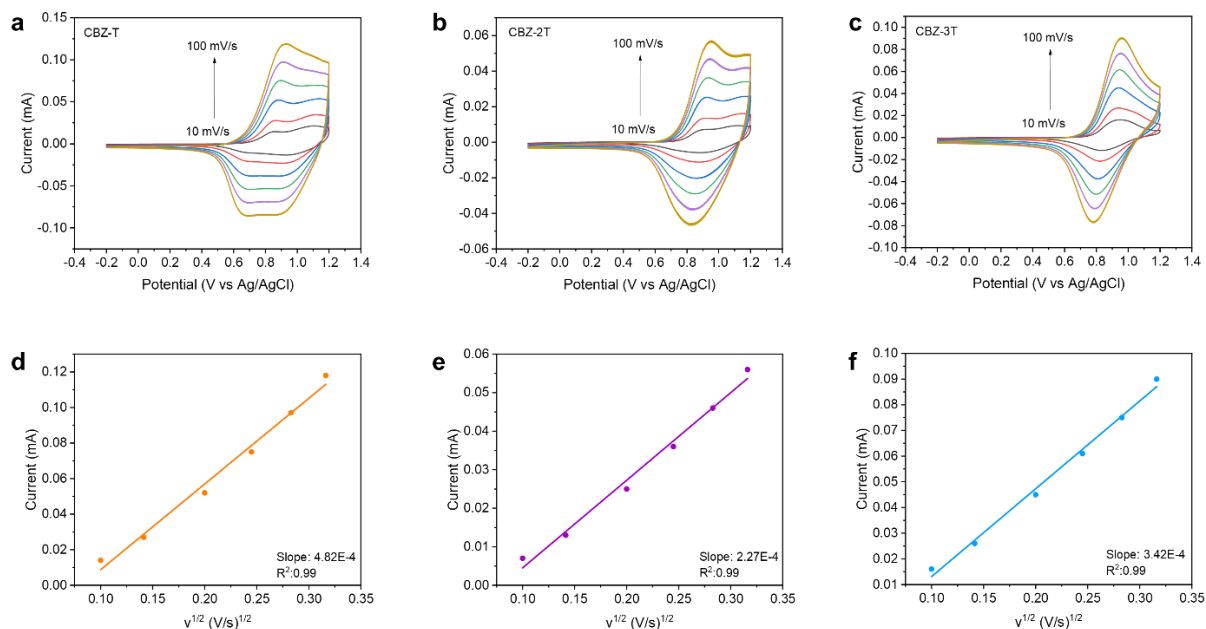


Figure S15. The thin film cyclic voltammograms of (a) CBZ-T1, (b) CBZ-T2, and (c) CBZ-T3 at different scan rates. Plots of the peak current vs. square root of the scan rates of (d) CBZ-T1, (e) CBZ-T2, and (f) CBZ-T3.

The diffusion coefficients (D) of polymer films were calculated from thin film CV using the Randles-Sevcik equation.

$$I_p = (2.6 \times 10^5) n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}}$$

Where I_p is the oxidation peak current, n is the number of electrons, A is the area of the electrode, C is the concentration of electrolyte, and v is the scan rate. The diffusion coefficients of CBZ-T1, CBZ-T2, and CBZ-T3 are $2.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $4.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and $1.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively.

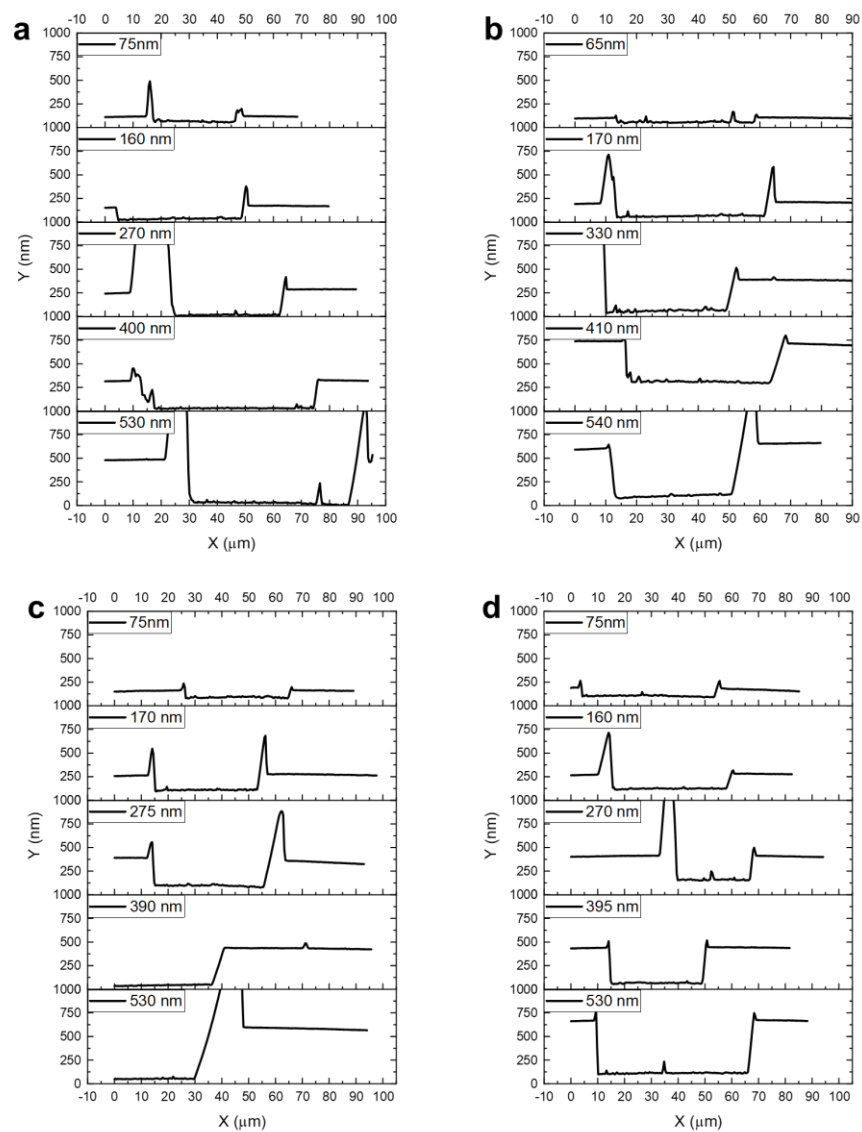


Figure S16. AFM film thickness measurement of (a) CBZ-T1, (b) CBZ-T2, (c) CBZ-T3, and (d) CBZ-Blend.

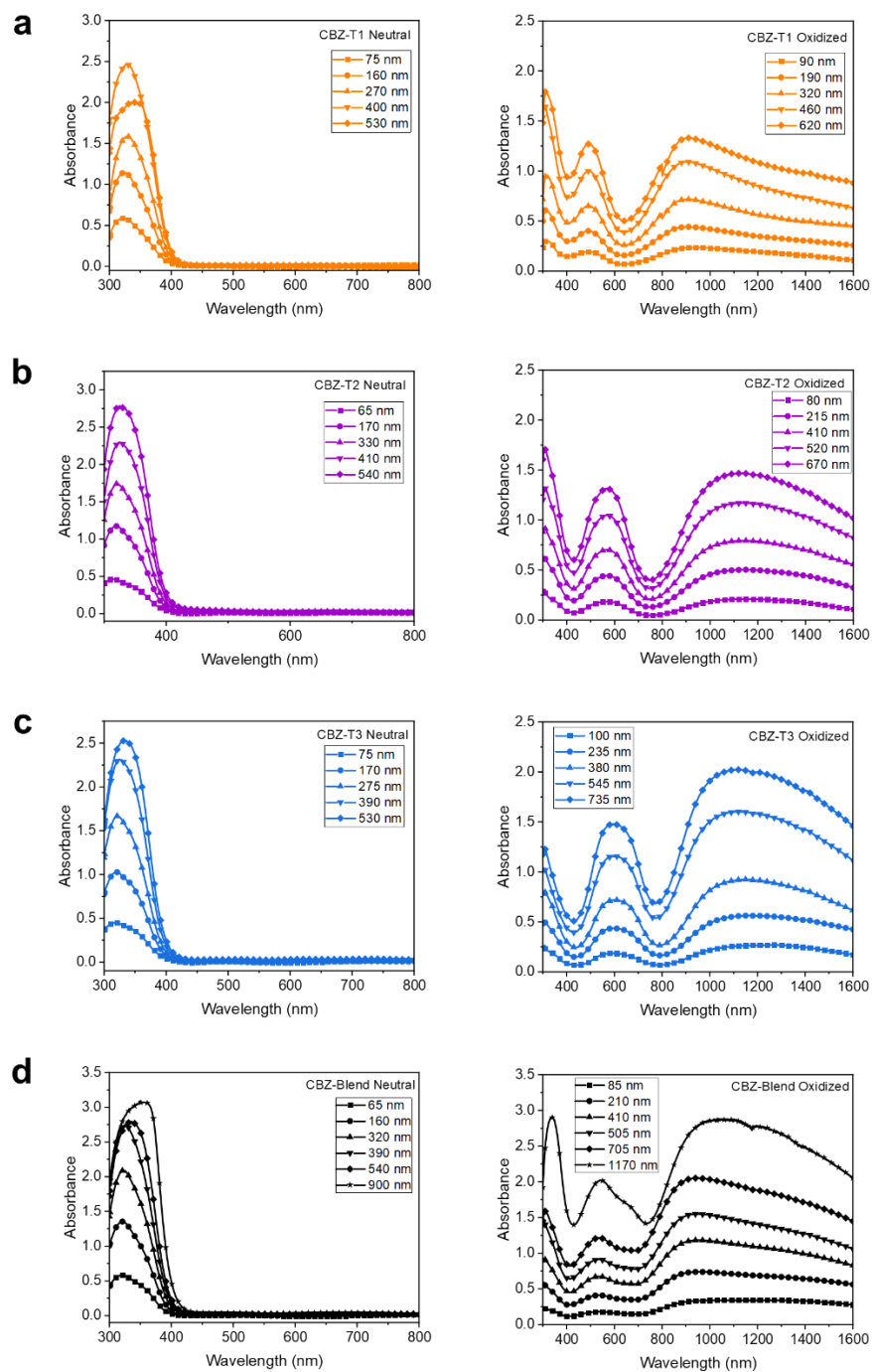


Figure S15. Absorption spectra of (a) CBZ-T1 (b) CBZ-T2 (c) CBZ-T3, and (d) CBZ-Blend polymer films with different film thickness in their neutral and oxidized states.

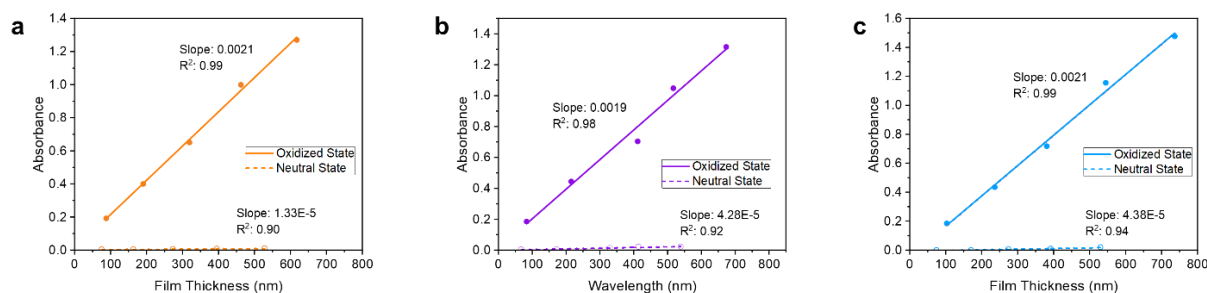


Figure S16. Beer-Lambert plots of (a) CBZ-T1 (b) CBZ-T2 (c) CBZ-T3 in their neutral (circle and dashed line) and oxidized (dots and solid line) states. The absorptions are from UV-Vis spectra and film thicknesses are measured by AFM.

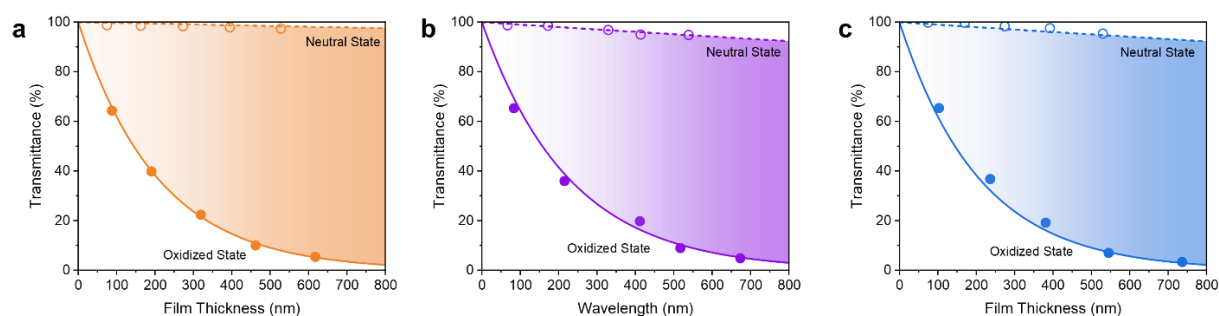


Figure S17. The transmittance of neutral and oxidized state versus film thickness for (a) CBZ-T1 (b) CBZ-T2, and (c) CBZ-T3

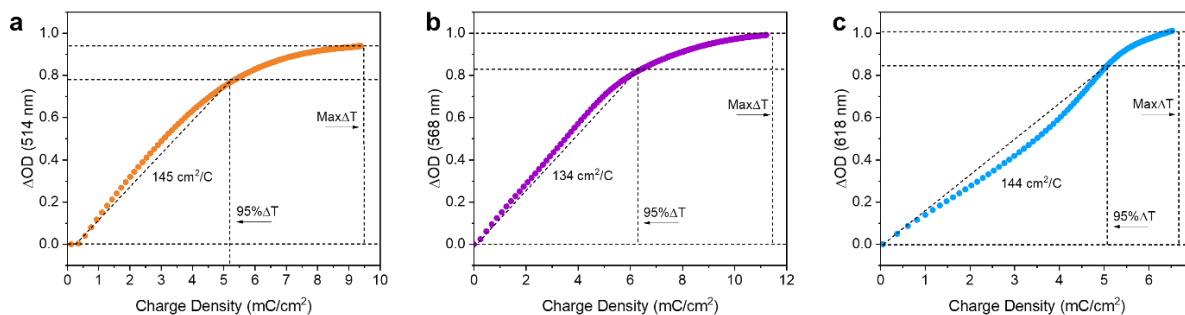


Figure S18. The composite coloration efficiency (95% of total transmittance) of (a) CBZ-T1, (b) CBZ-T2, and (c) CBZ-T3

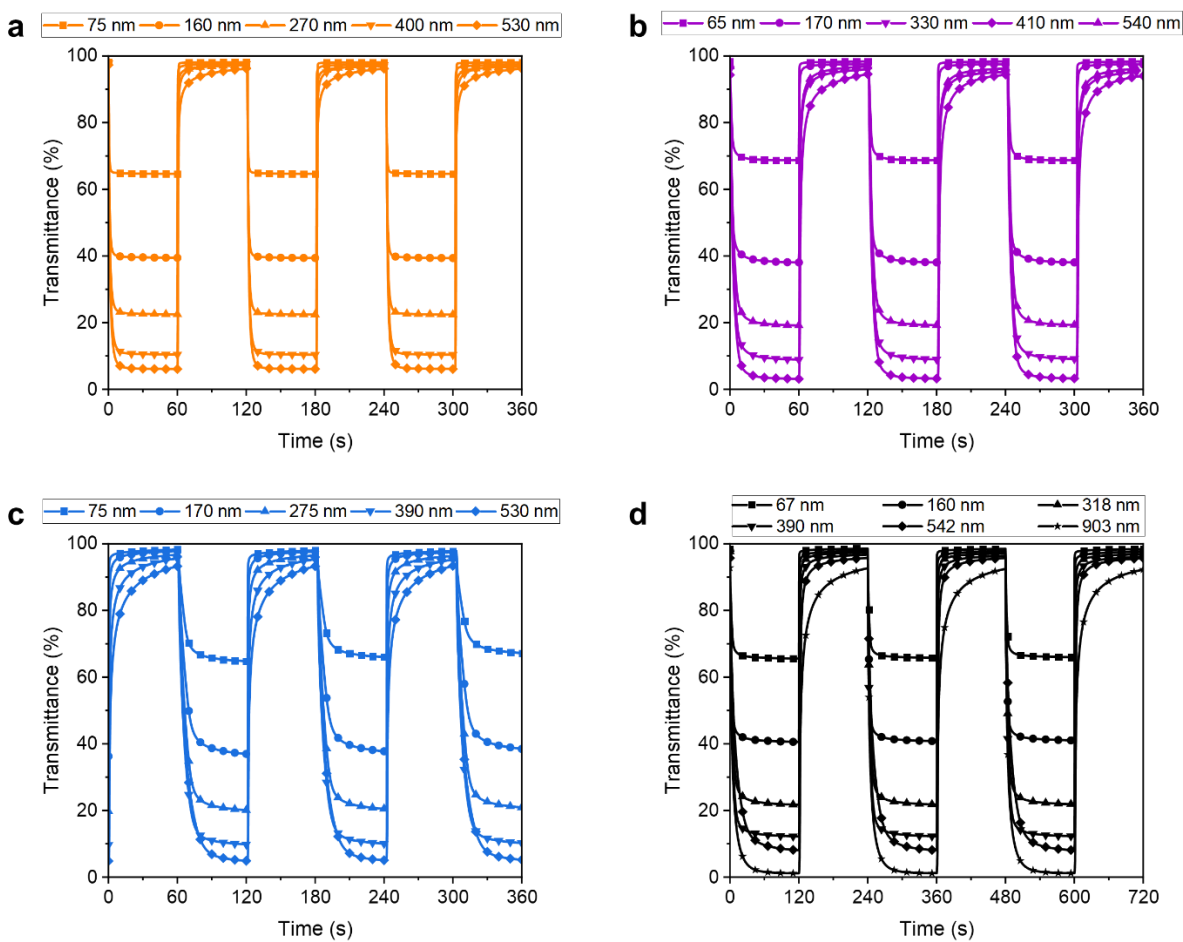


Figure S19. Switching kinetics of (a) CBZ-T1 (b) CBZ-T2 (c) CBZ-T3 and (d) CBZ-Blend films at different thickness. The transmittance is measured at $\lambda_{\max}$

2.5 Optical modeling

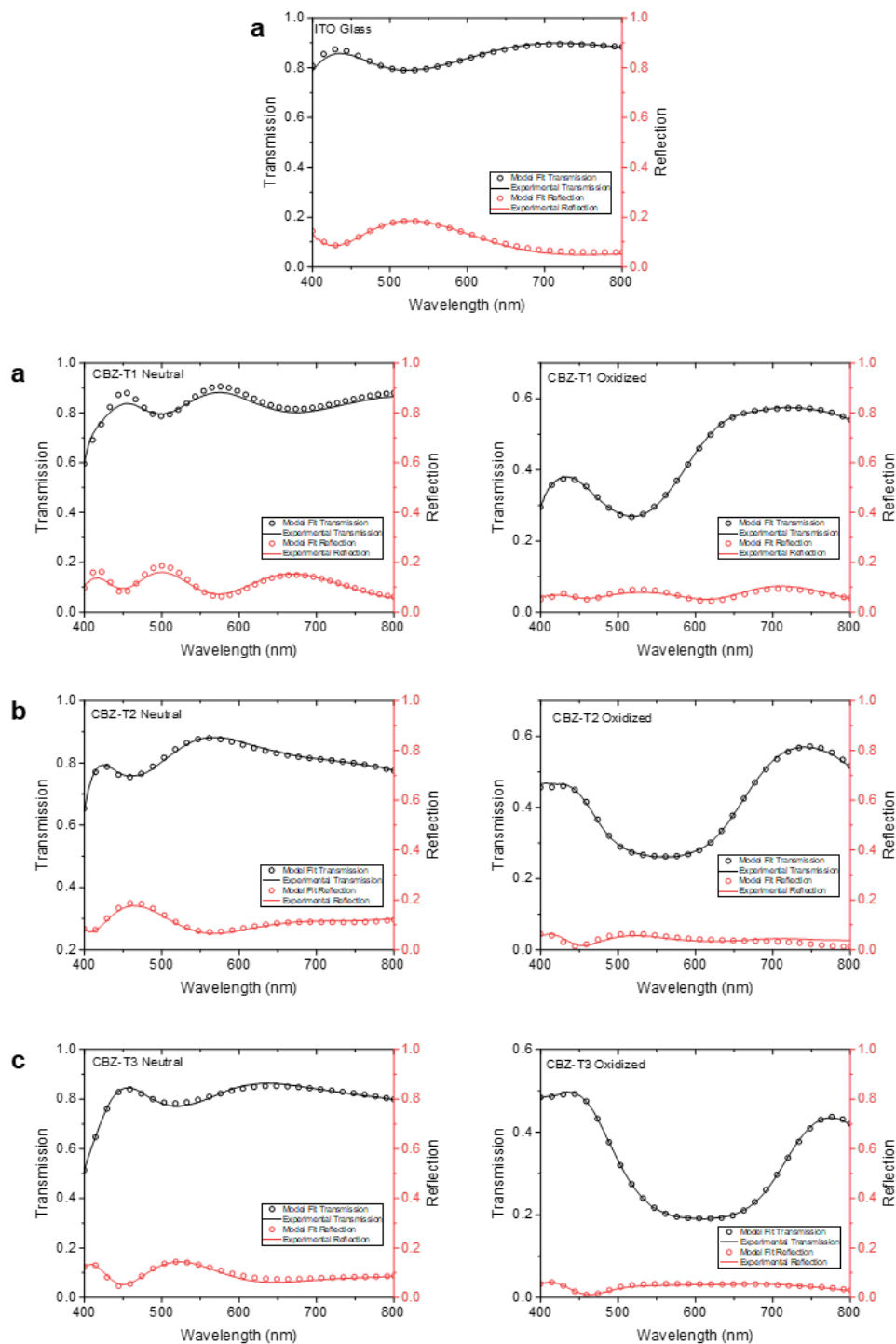


Figure S20. Generated model vs. experimental data for transmission and reflection of (a) ITO glass, (b) CBZ-T1, (c) CBZ-T2, and (d) CBZ-T3.

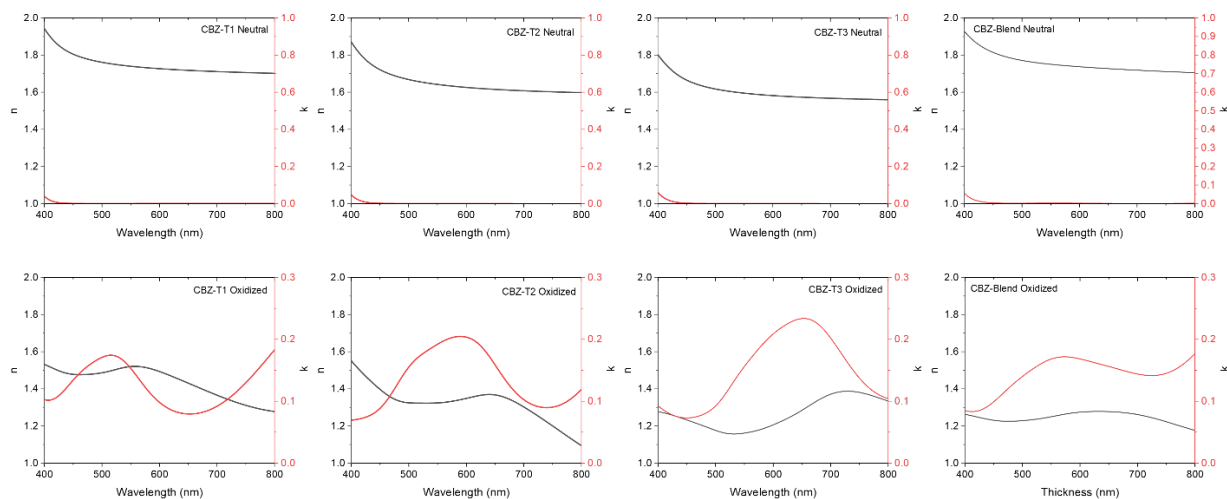


Figure S21. The refractive index (n) and extinction coefficient (k) of the meta-conjugated polymers are in both neutral and oxidized state.

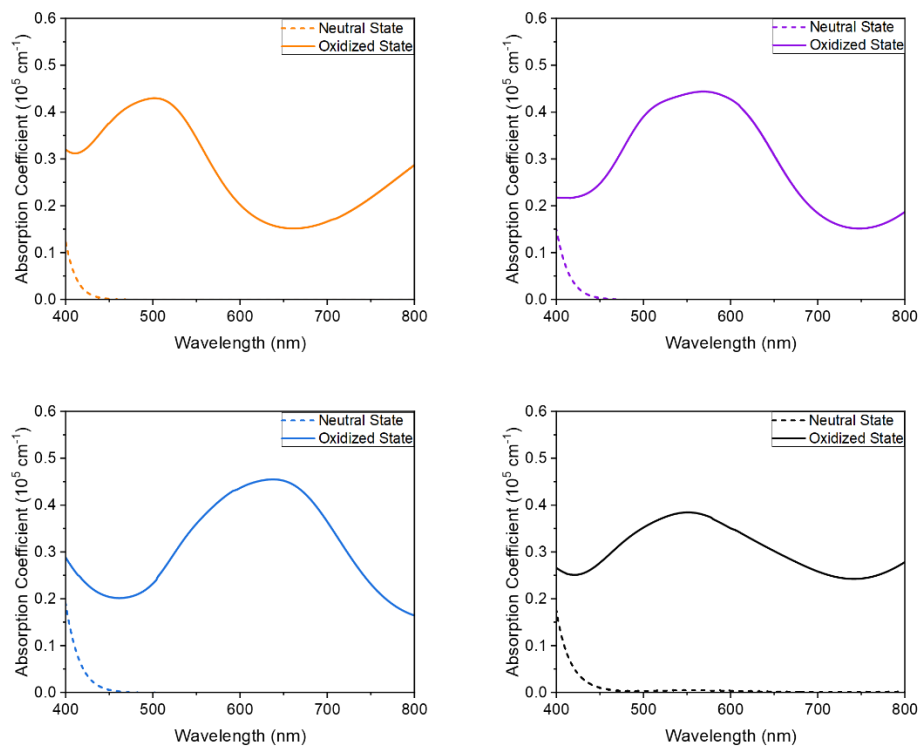


Figure S22. The absorption coefficient of (a) CBZ-T1 (b) CBZ-T2 (c) CBZ-T3 and (d) CBZ-Blend

2.6 Thin Film Stability

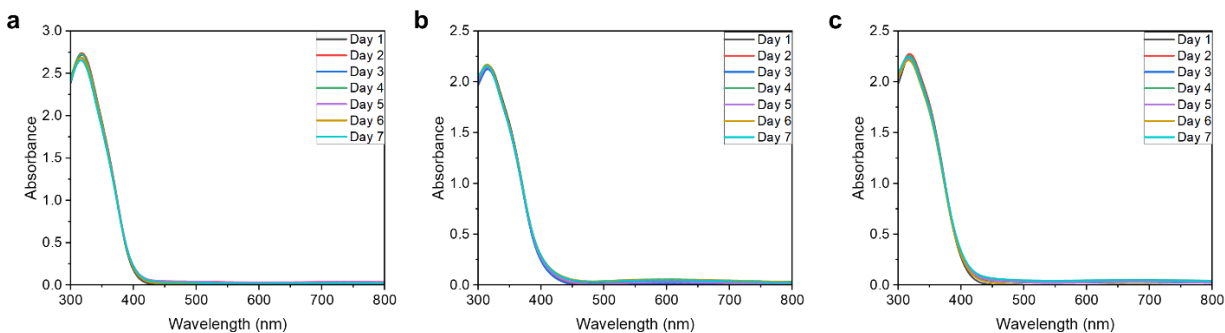


Figure S23. The absorption spectra of (a) CBZ-T1, (b) CBZ-T2, and (c) CBZ-T3 film samples after the photostability testing for 7 days in the weathering chamber equipped with Xe-arc lamps and a daylight filter for AM 1.5 solar spectrum and 1000 W/cm² light irradiance.

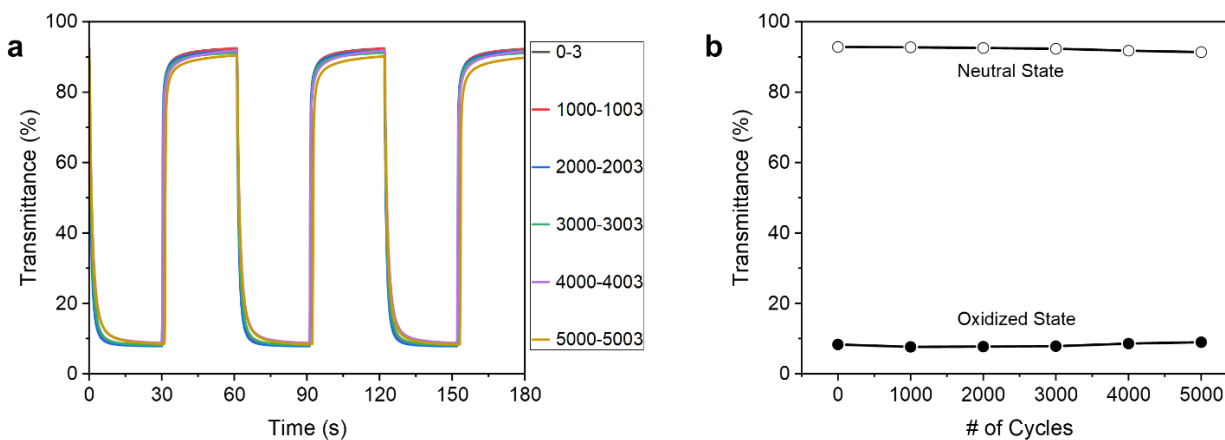


Figure S24. (a) Switching kinetics CBZ-Blend measured at 550 nm for 5000 cycles. (b) Transmittance at 550 nm every 1000 cycles.

2.7 Device performance

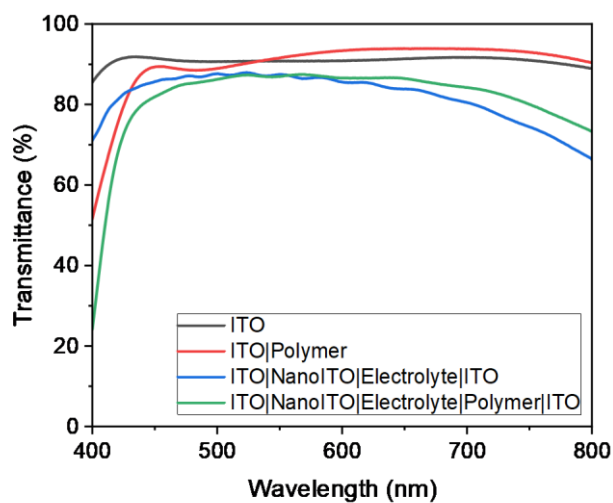


Figure S25. Transmittance spectra of each layer of the Transparent-to-black device.

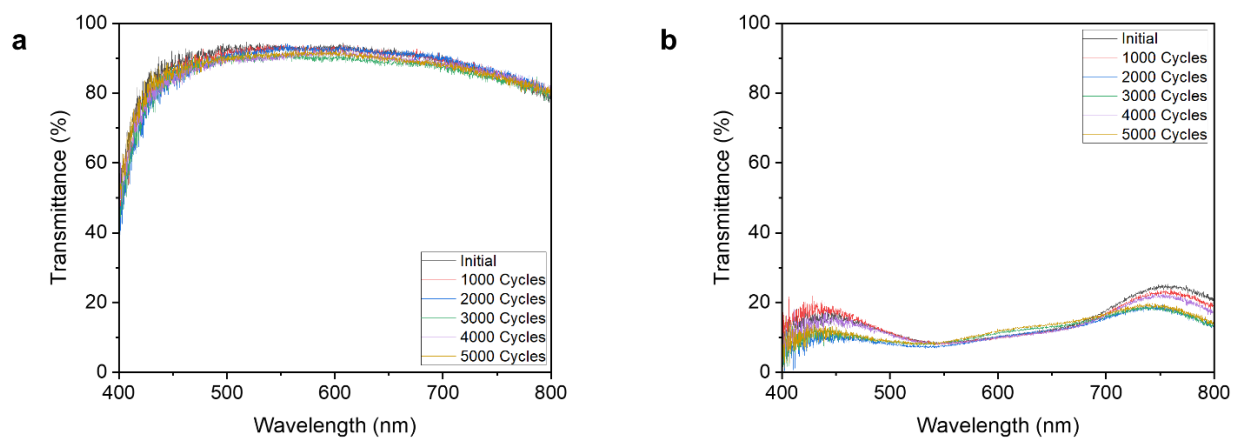


Figure S26. The transmittance spectra of Transparent-to-black electrochromic device under -0.6 V for (a) Transparent states, and 2.4 V for (b) colored states over 5000 cycles.

3. Supplementary Tables

Supplementary Table 1. Summary of GPC results

ECP	Mn (kDa)	Mw (kDa)	PDI
CBZ-T1	7.22	29.45	4.08
CBZ-T2	12.94	59.27	4.58
CBZ-T3	14.91	32.01	2.15
BP-T1	11.63	65.99	5.67
BP-T2	13.97	66.95	4.79
BP-T3	29.06	64.95	2.23
BNP-T1	8.22	27.97	3.40
BNP-T2	7.88	14.74	1.87
BNP-T3	18.72	38.52	2.06

Supplementary Table 2. Summary of calculated dihedral angles (δ) of all polymers in their neutral (N) and radical cation (RC) state.

ECP	δ_1		δ_2		δ_3		δ_4	
	N	RC	N	RC	N	RC	N	RC
CBZ-T1	52.51	27.67	51.21	24.45	-	-	-	-
CBZ-T2	49.52	33.44	49.31	32.93	78.92	6.7	-	-
CBZ-T3	49.06	39.99	49.92	37.08	78.87	25.3	79.04	27.01
BP-T1	48.80	26.84	48.44	24.39	-	-	-	-
BP-T2	48.90	36.25	48.16	34.54	76.21	1.47	-	-
BP-T3	49.98	42.83	50.02	43.17	99.80	17.51	80.92	17.41
BNP-T1	48.98	26.62	48.59	23.64	-	-	-	-
BNP-T2	50.48	38.82	50.63	40.88	83.76	8.96	-	-
BNP-T3	45.88	43.70	46.94	38.62	77.26	20.16	77.09	15.17

Supplementary Table 3. The optical and electrochemical properties of meta-conjugated electrochromic polymers.

ECP	λ_{onset} (nm) ^a	λ_{max} (nm) ^b	E_{onset} (V) ^c
CBZ-T1	390	514	0.65
CBZ-T2	391	568	0.70
CBZ-T3	390	618	0.69
BP-T1	360	480	0.87
BP-T2	374	540	0.82
BP-T3	378	592	0.82
BNP-T1	390	560	0.87
BNP-T2	391	570	0.86
BNP-T3	392	600	0.85

^a The absorption onset wavelength in neutral state.

^b The maximum absorption wavelength in oxidized state.

^c The voltage is reference to Ag/AgCl.

Supplementary Table 4. Slopes of the Beer-Lambert plots of polymer thin films and conversion to absorption coefficient in oxidized state of the polymers.

ECP	Slope of the Beer-Lambert Plot ($\times 10^5$ cm ⁻¹)	Absorption coefficient from Beer-Lambert Plot ($\times 10^5$ cm ⁻¹)	Absorption coefficient from optical modeling ($\times 10^5$ cm ⁻¹)
CBZ-T1	0.21	0.48	0.43
CBZ-T2	0.19	0.44	0.46
CBZ-T3	0.21	0.48	0.45
CBZ-Blend	0.16	0.37	0.38

4. Reference

1. K. Morimoto, T. Nakae, N. Yamaoka, T. Dohi, and Y. Kita, *Eur. J. Org. Chem.*, 2011, 6326.
2. Fitzner,R.; Mena-Osteritz,E.; Mishra,A.; Schulz,G.; Reinold,E.;Weil,M.; Körner,C.; Ziehlke,H.; Elschner,C.; Leo,K.; et al.. *J. Am. Chem.Soc.* 2012, 134, 11064–11067